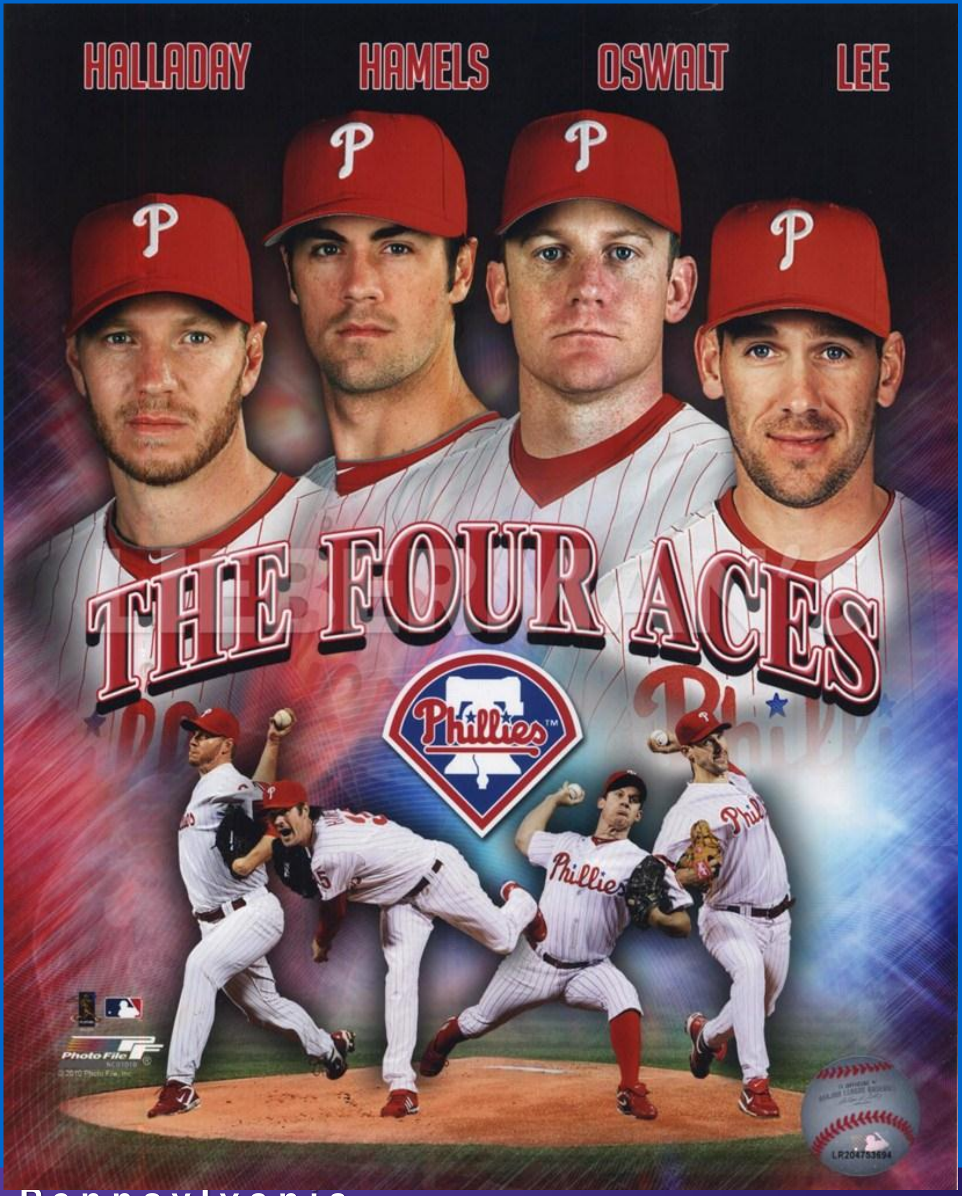
Advanced Colloids Experiment

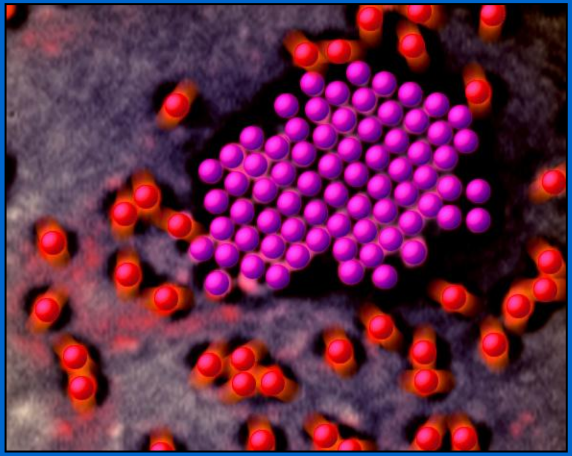
LΦCA (Phase 2) Science Concept Review

June 14, 2011

PHOUR ACES IN PHILADELPHIA



LΦCA (Phase 2)



Arjun Yodh (PI)
Peter Yunker (Co-I)
Tim Still (Co-I)
Ke Chen (Co-I)
Matt Gratale (Co-I)

Department of Physics & Astronomy
University of Pennsylvania
Philadelphia, PA 19104-6396

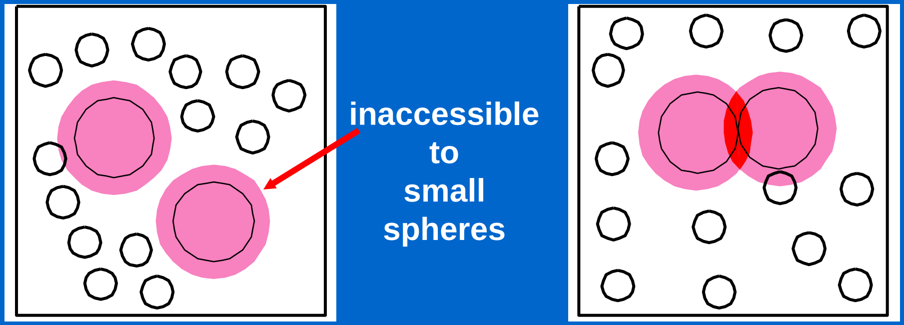
Bill Meyer
NASA Project Scientist

Overview

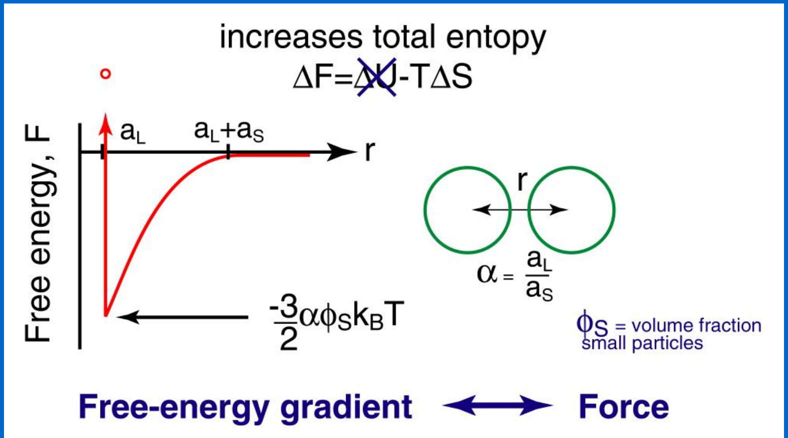
- Reminders about Original (approved) LΦCA
  - What was planned?
  - Why was it valuable?
- Progress & Evolved Goals
- New Science Background (including objectives for microgravity)
  - Assembly of Anisotropic Particles
  - Disorder-induced Crystal-Glass Transitions
  - Jamming Phenomenology
  - Other Interesting Experiments
  - Microgravity Justification
- Experimental Concepts & Science Requirements

Reminders about Original (Approved) LΦCA:
Entropic Forces and Colloidal Epitaxy

Depletion Force:

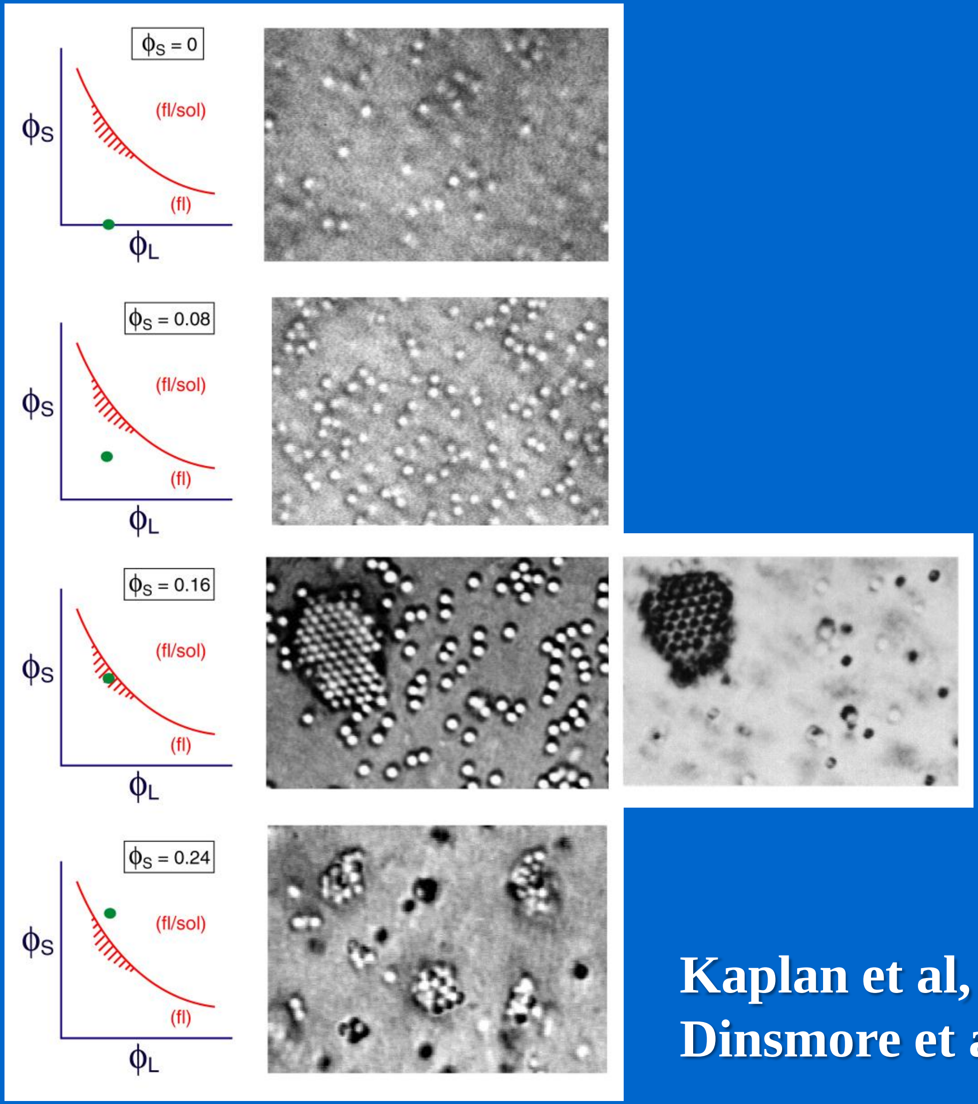


→ **Moving 2 large spheres together increases volume accessible to small spheres**



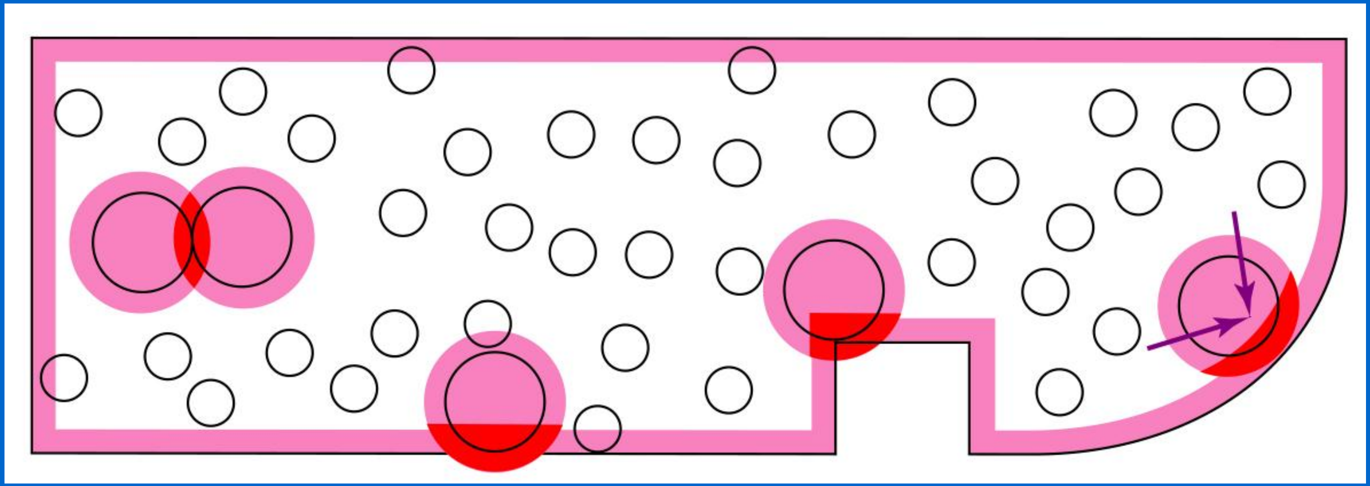
Asakura, S.; Oosawa, S. *J. Polym. Sci., 1958;* Vrij, A. *Pure Appl. Chem., 1976.*

RANGE OF COMPOSITIONS WHERE "EQUILIBRIUM" COLLOIDAL EPITAXY IS POSSIBLE!

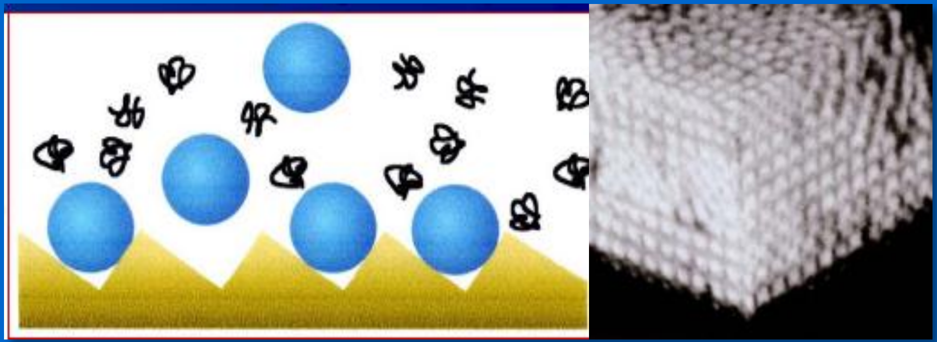


Kaplan et al, PRL, 1994
Dinsmore et al, EPL, 1997

Reminders about Original (Approved) LΦCA



Kaplan et al, PRL, 1994
Dinsmore et al, PR E, 1995
Dinsmore et al, Nature ,1996
Dinsmore et al, EPL, 1997
Dinsmore et al, PRL, 1998
Verma et al, PRL, 1998
Crocker et al, PRL, 1999
Dinsmore et al, Langmuir, 1999
Verma et al, Macromolecules, 2000



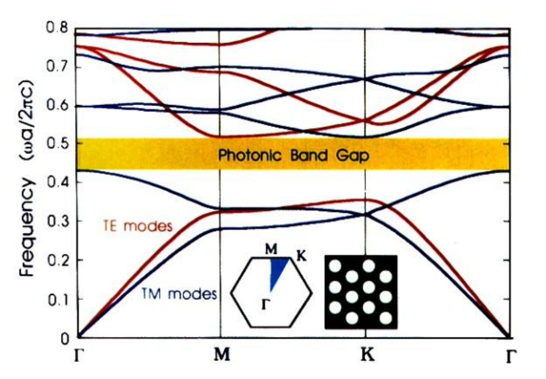
Lin et al, PRL , 2000

COLLOIDAL ASSEMBLY

Entropic assembly in non-ideal systems without complications of sedimentation, creaming and the associated hydrodynamics.

- **Definitive set of "entropic" phase-diagrams for particles with more complex interactions.**
- **Open structures.**
- **Affects of doping on crystallization.**

PHOTONICS



NEW MACROPOROUS MATERIALS

FINAL CHOICE OF PARTICLES TO BE MADE CLOSER TO FLIGHT TIME.
TENTATIVE PARTICLE CHOICES (many particle-types to choose from).

Objectives for the Spaceflight Experiment

(1) To synthesize and stabilize a variety of novel high- and low-density particles in aqueous and organic suspensions. The motivation for the synthesis of these particle types derives entirely from our proposed assembly experiments in microgravity.

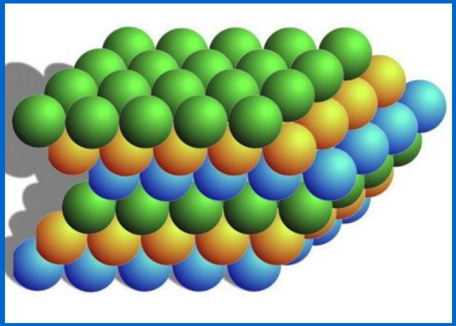
(2) To determine the conditions (e.g. volume fractions, size ratios, etc.) for which colloidal crystals composed of these novel particles can be grown entropically in microgravity. This growth will exploit depletion-driven attractive interactions and surface templates. The experiments represent the first thermodynamic observations of these novel systems; they will provide insight about interparticle interactions that are normally masked by sedimentation, and it is possible that more "open" crystalline structures can be induced to form in microgravity.

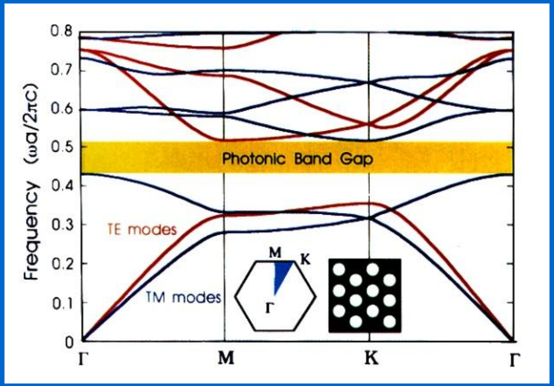
Why interesting?

- **Fundamental Statistical Physics & Colloid Science**
  - What structures can we build (shape, interaction, etc.)?
  - Can we understand phase behaviors better?
  - What happens “near” dynamic arrest?
  - Non-ideal particles (real systems)

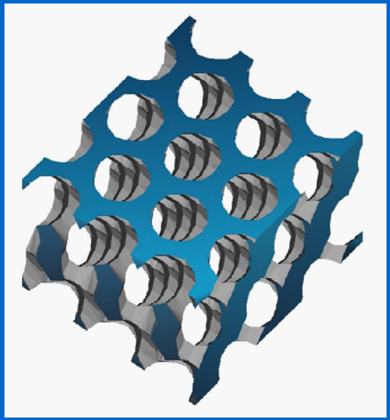
New Materials with Novel Optical Properties

- **Three-dimensionally periodic dielectric materials alter the local density of states for photons.**





***Direct Structures**



Inverse Structures

Affects of disorder, doping, novel background materials in direct structures, ... ?
Few photonic bandstructure measurements in high-contrast direct structures.

New Macroporous Materials

Catalytic surfaces and supports.

Separation and absorbent media.

New Chromatographic Materials.

Macromolecular diffusion through colloidal arrays?!

- **Exotic Media**

  Ordered arrays of superconducting and/or metal particles

  Statistical Physics of Vortex Lattices in arrays of SC particles.

Evolving Projects

Entropically Driven Self-Assembly is still interesting for colloid engineering in microgravity, for new materials, & for fundamental science. (Experiments are still doable!)

But – exciting new developments "happened" while waiting.

Forethought of NASA to make "versatile" microscope facilities in space now enable scientists to adapt programs towards "latest/best" research.

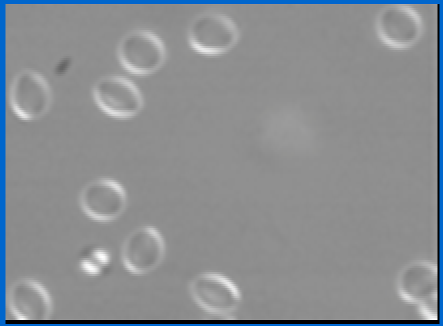
Evolved Projects: Interesting for Many of the Same Reasons!

- **Fundamental Statistical Physics & Colloid Science**
  - What structures can we build (shape, interaction, etc.)?
  - Can we understand phase behaviors better?
  - What happens “near” dynamic arrest?
  - Non-ideal particles (real systems)
  - New Materials

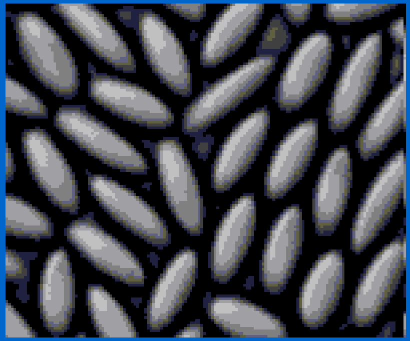
    - Unmask effects of sedimentation and creaming.
    - Experiments with “useful” index matched systems that are not easily density matched.
    - Pioneering colloid engineering in microgravity.

What's new in our lab?

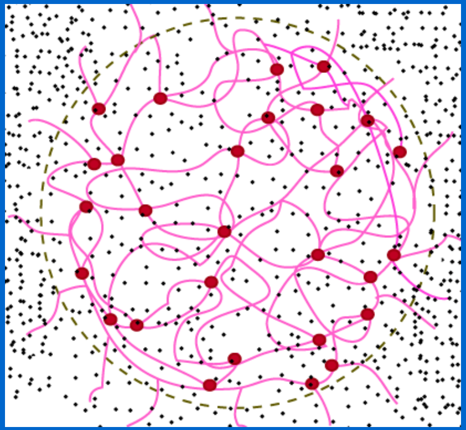
- Particles!



Discs



Ellipsoids



Temperature-sensitive particles

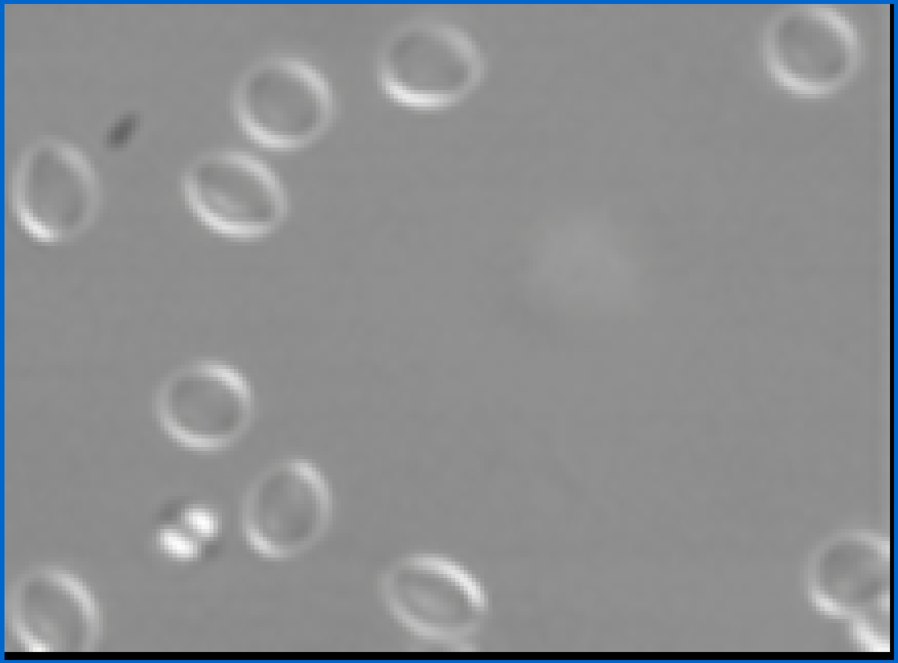
ALSO: PMMA-PS-Silica/NIPA particles

And Physics derived using these particles!

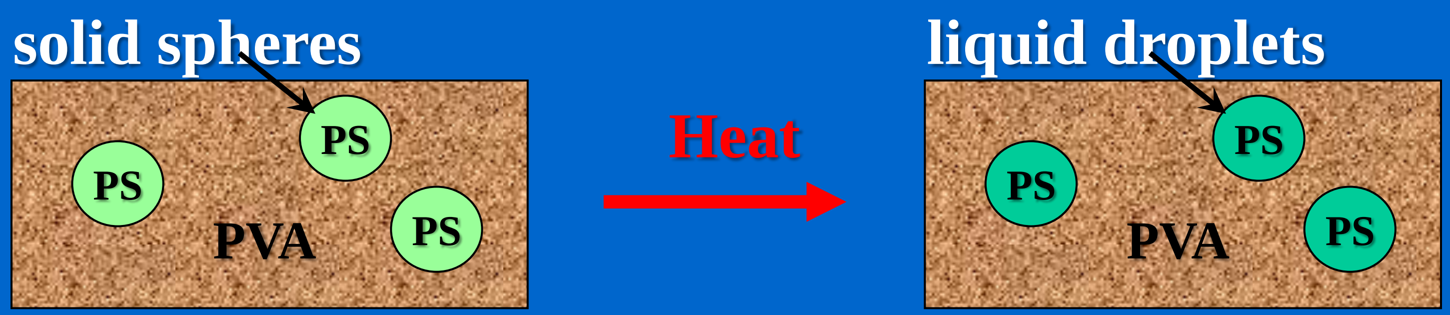
Ellipsoids & Discs

- New phases of matter
- New phase behavior/transitions.
- Glasses (2D) composed of Anisotropic Particles
  - Modes (Yunker et al, PR E 2010)
- Jamming

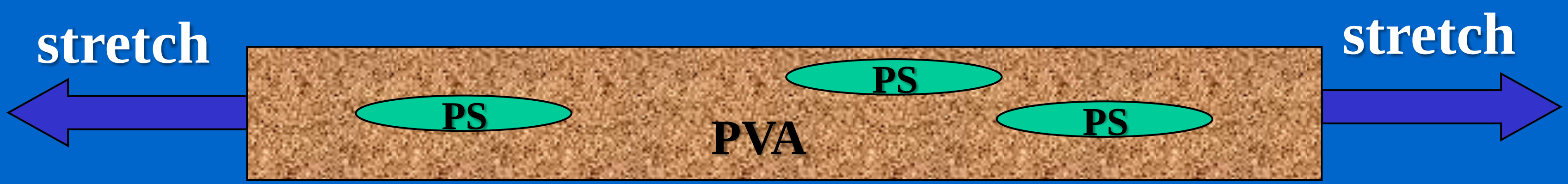
Discs



Stretch PS Spheres into Ellipsoids

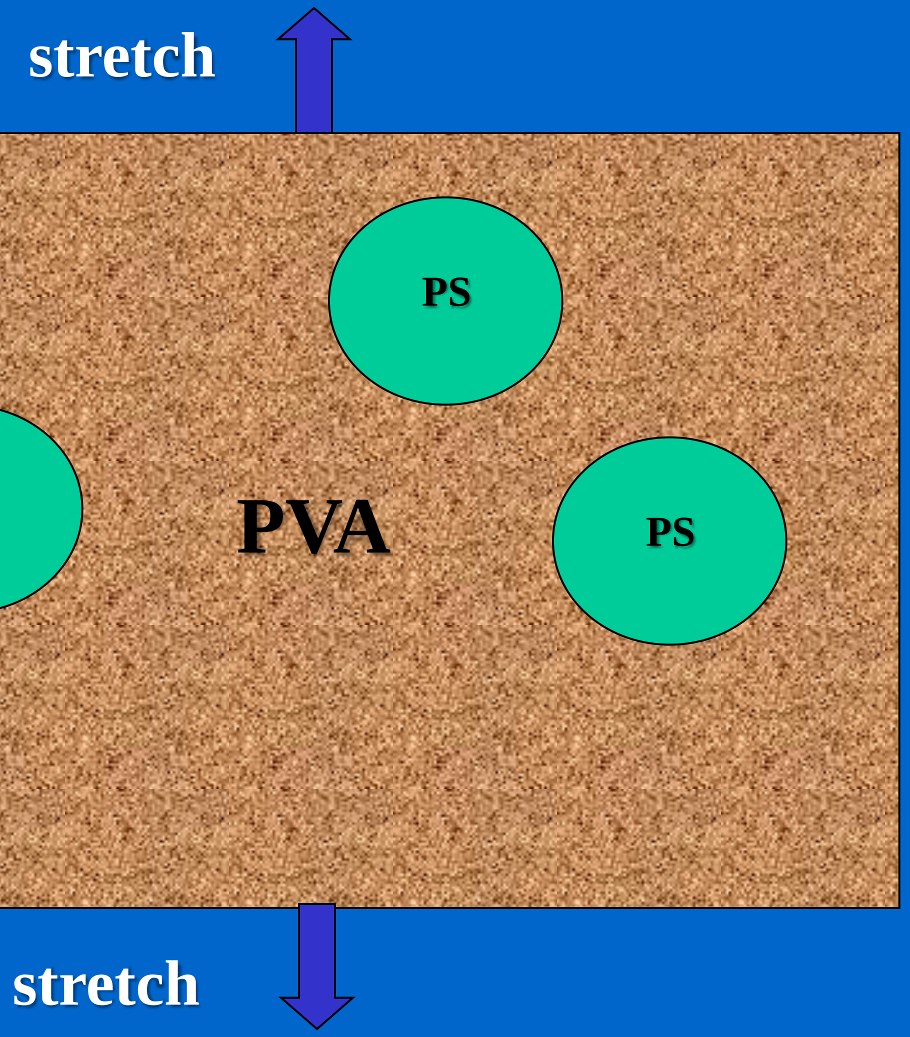


T_g (PS) < T ≈ 120°C < T_g (PVA)



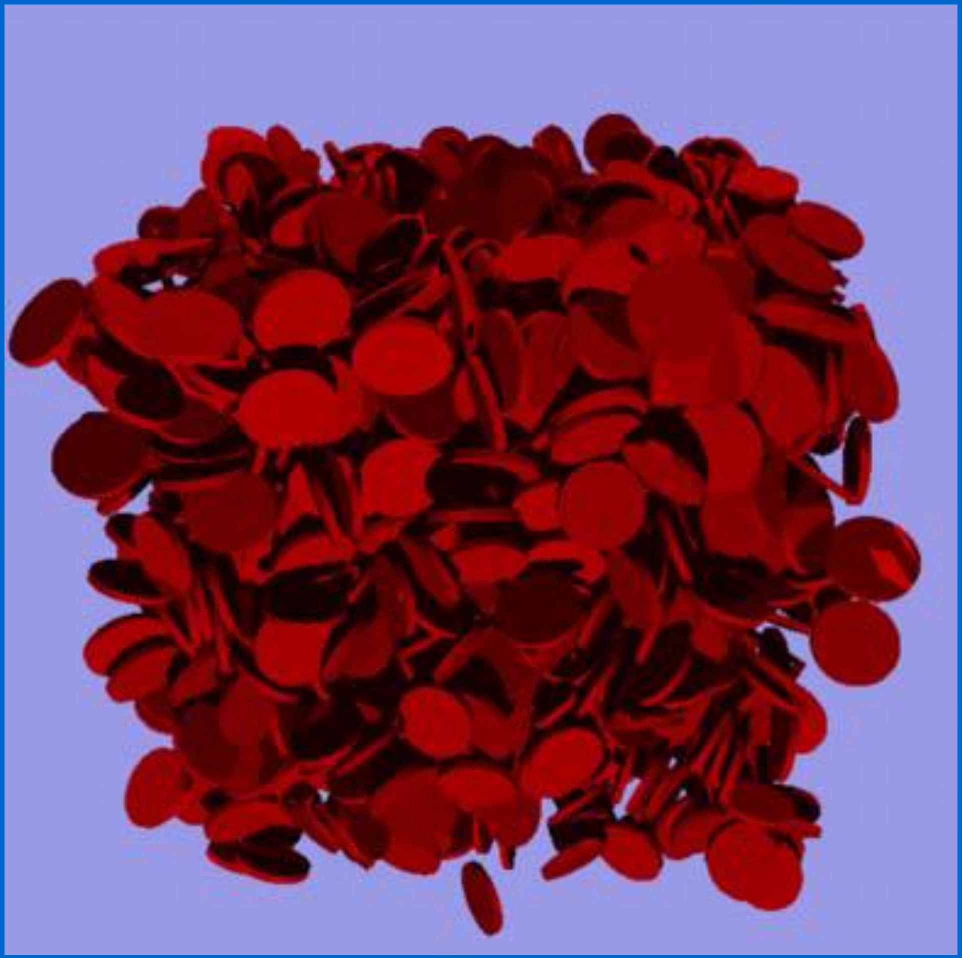
B. Felder, Helvetica Chimica Acta (1966).
C. C. Ho, et al., Colloid and Polymer Science (1993).
J. A. Champion, Y. K. Katare, and S. Mitragotri, PNAS (2007).

Stretch PS Spheres into Discs



Particle-types/Solvents are fixed: Difficult to Density Match

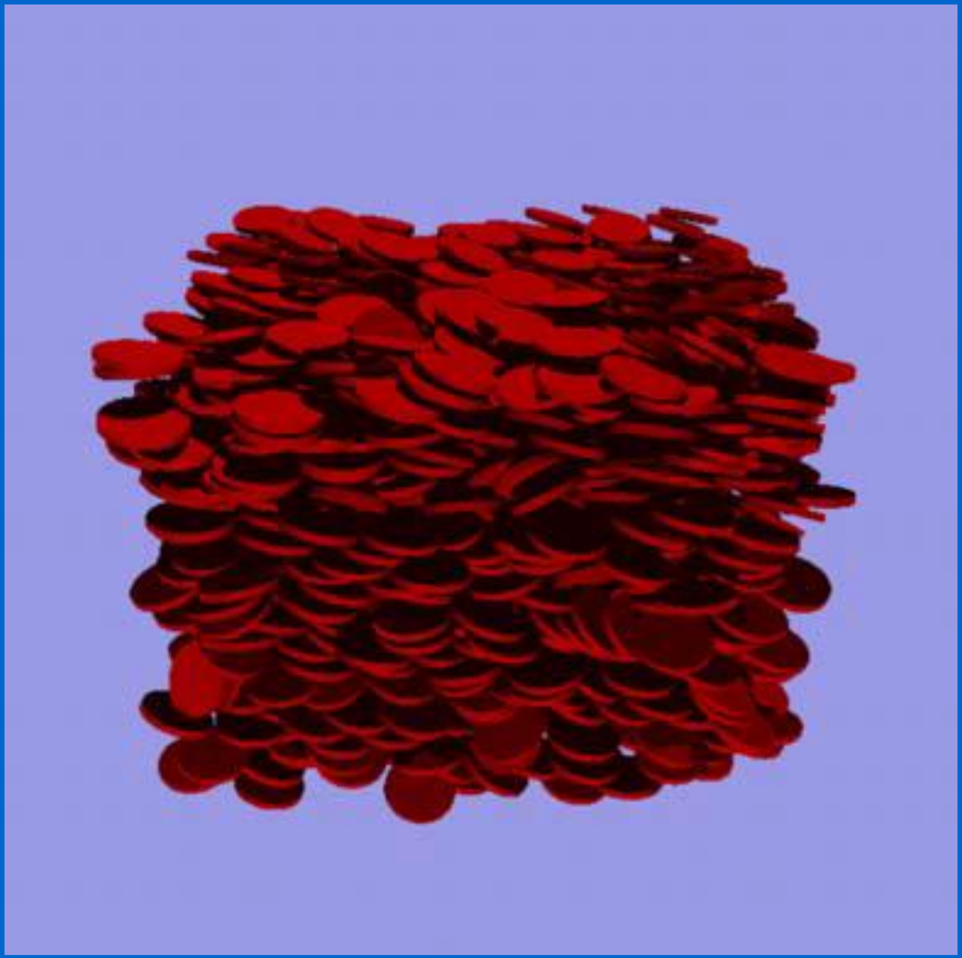
Isotropic Phase (Simulation)



P. D. Duncan, *et al.* PRE (2009)

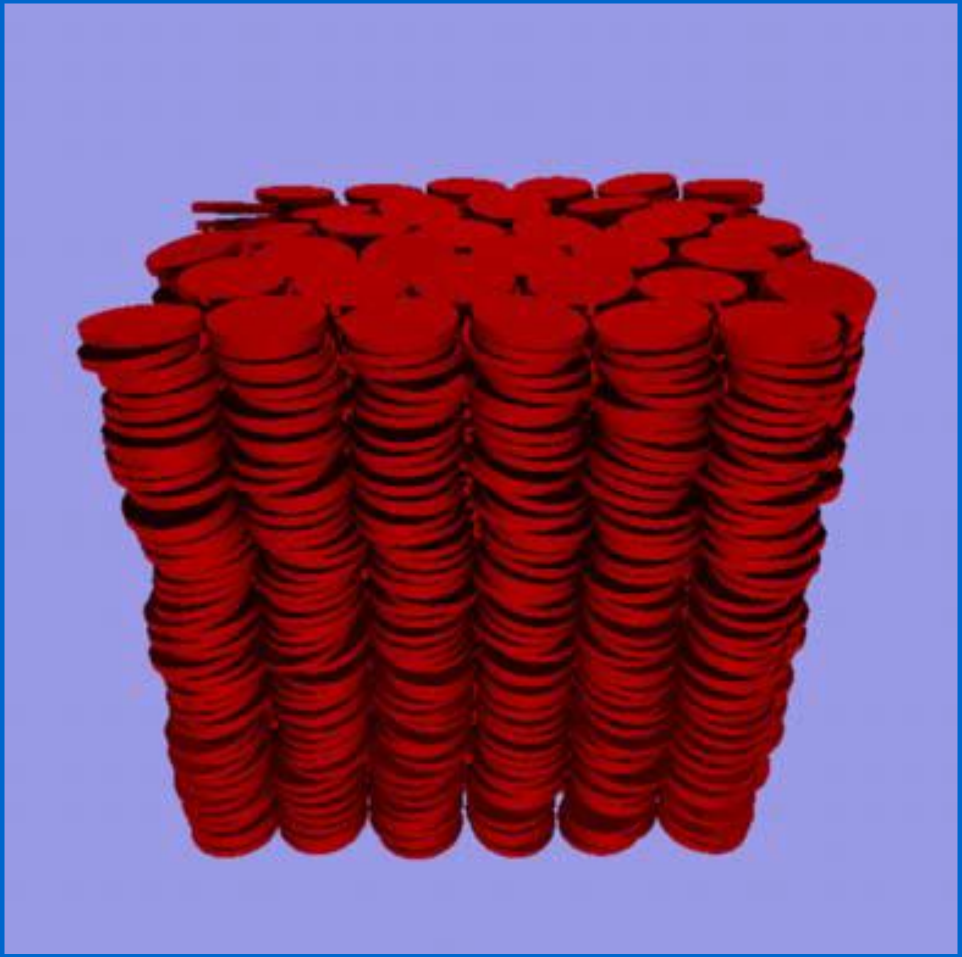
Disc-like cut spheres

Nematic Phase (Simulation)



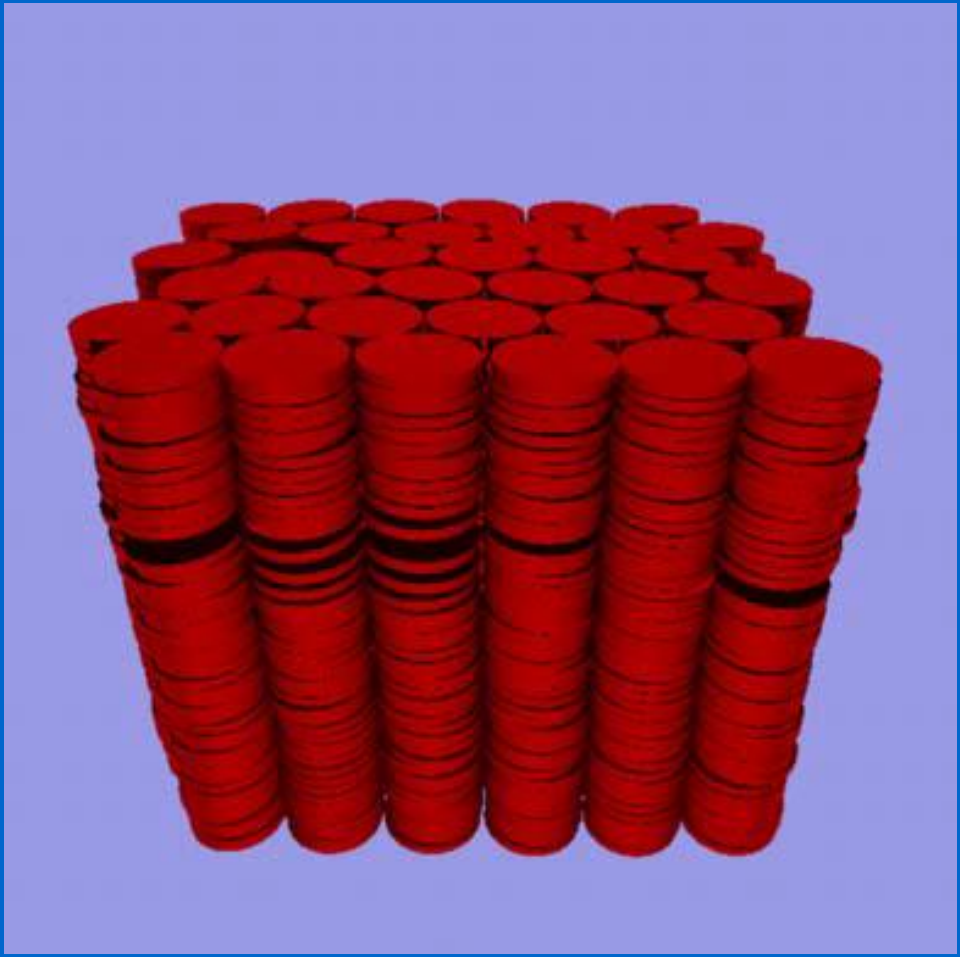
P. D. Duncan, *et al.* PRE (2009)

Columnar Phase (Simulation)



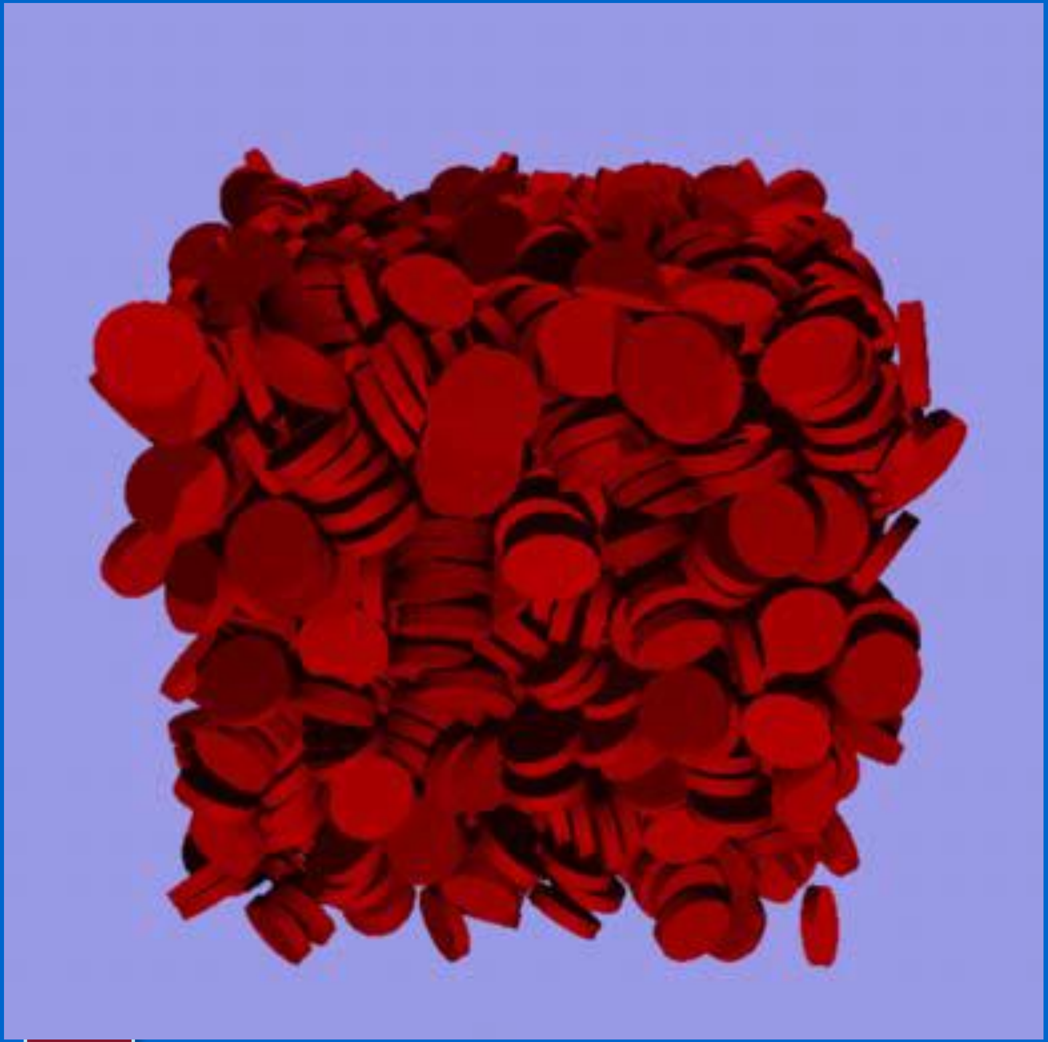
P. D. Duncan, *et al.* PRE (2009)

Solid Phase (Simulation)



P. D. Duncan, *et al.* PRE (2009)

Cubatic Phase (Simulation)



P. D. Duncan, *et al.* PRE (2009)

Oriented Stacks of 4-5 discs.
Neighboring Stacks are perpendicular.
Long-range orientational order.

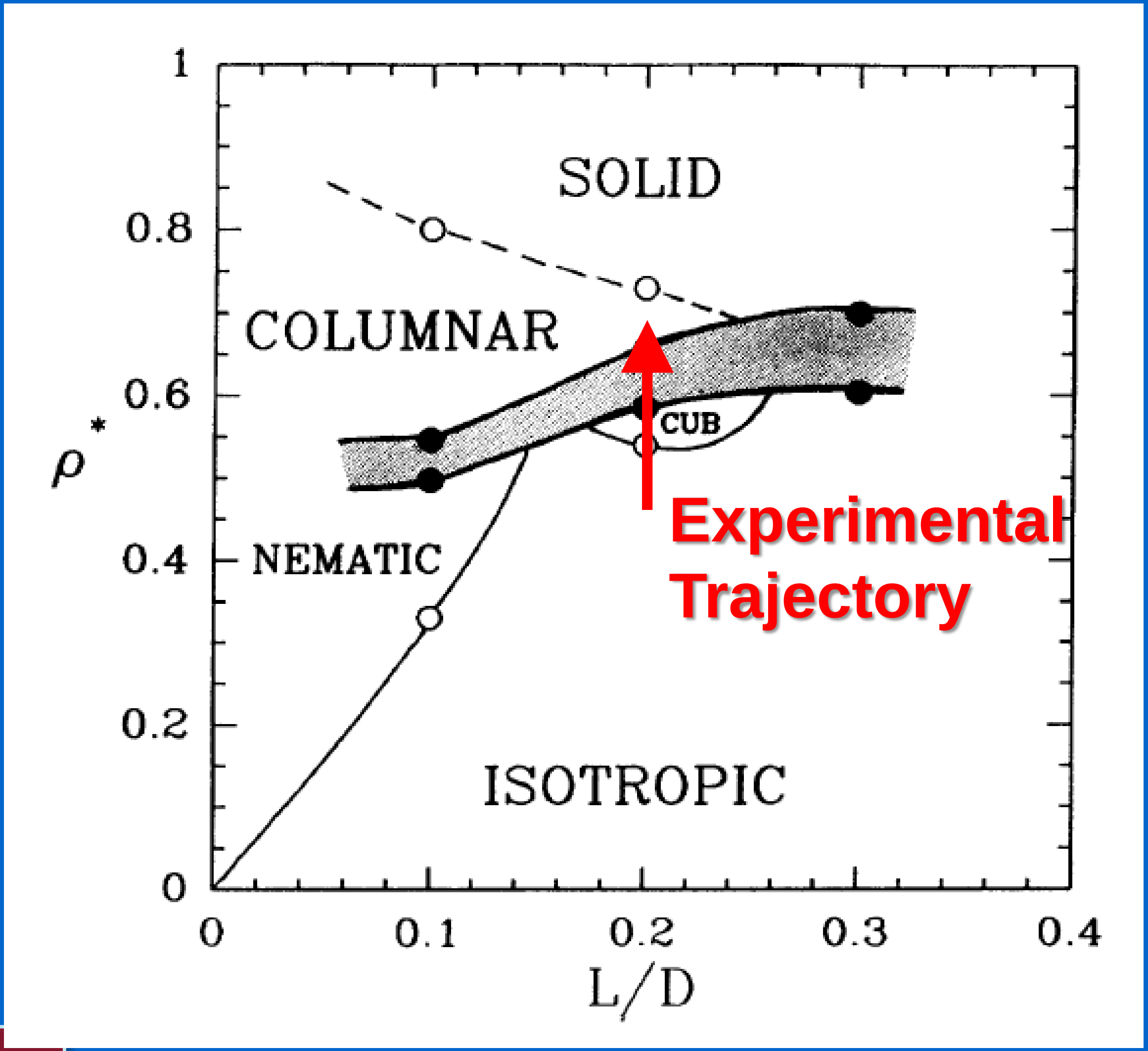
Predicted*. Some experimental evidence, but ambiguities persist.

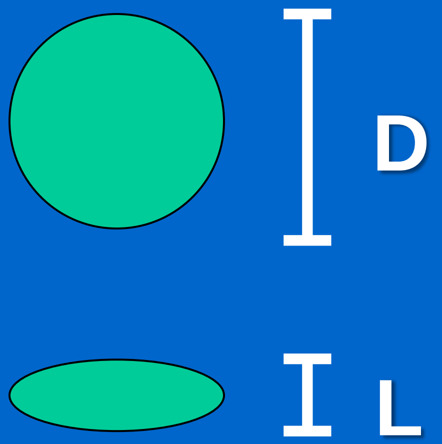
Model experiments with direct in-situ visualization are desirable.

Why so hard to find?
(Microgravity eliminates sedimentation issues)

***Veerman, Frenkel PRA (1992)**

Cubatic Phase Diagram

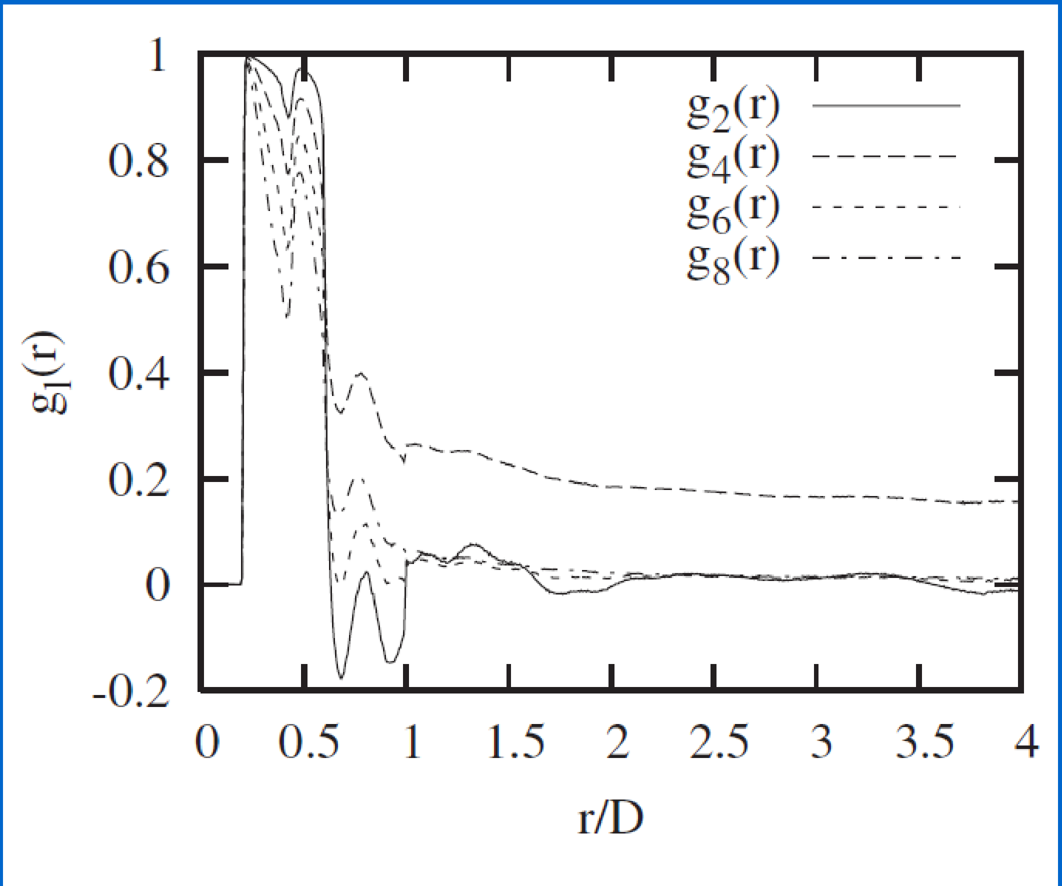




Search for phase in Ace-1A.

Veerman and Frenkel PRA (1992)

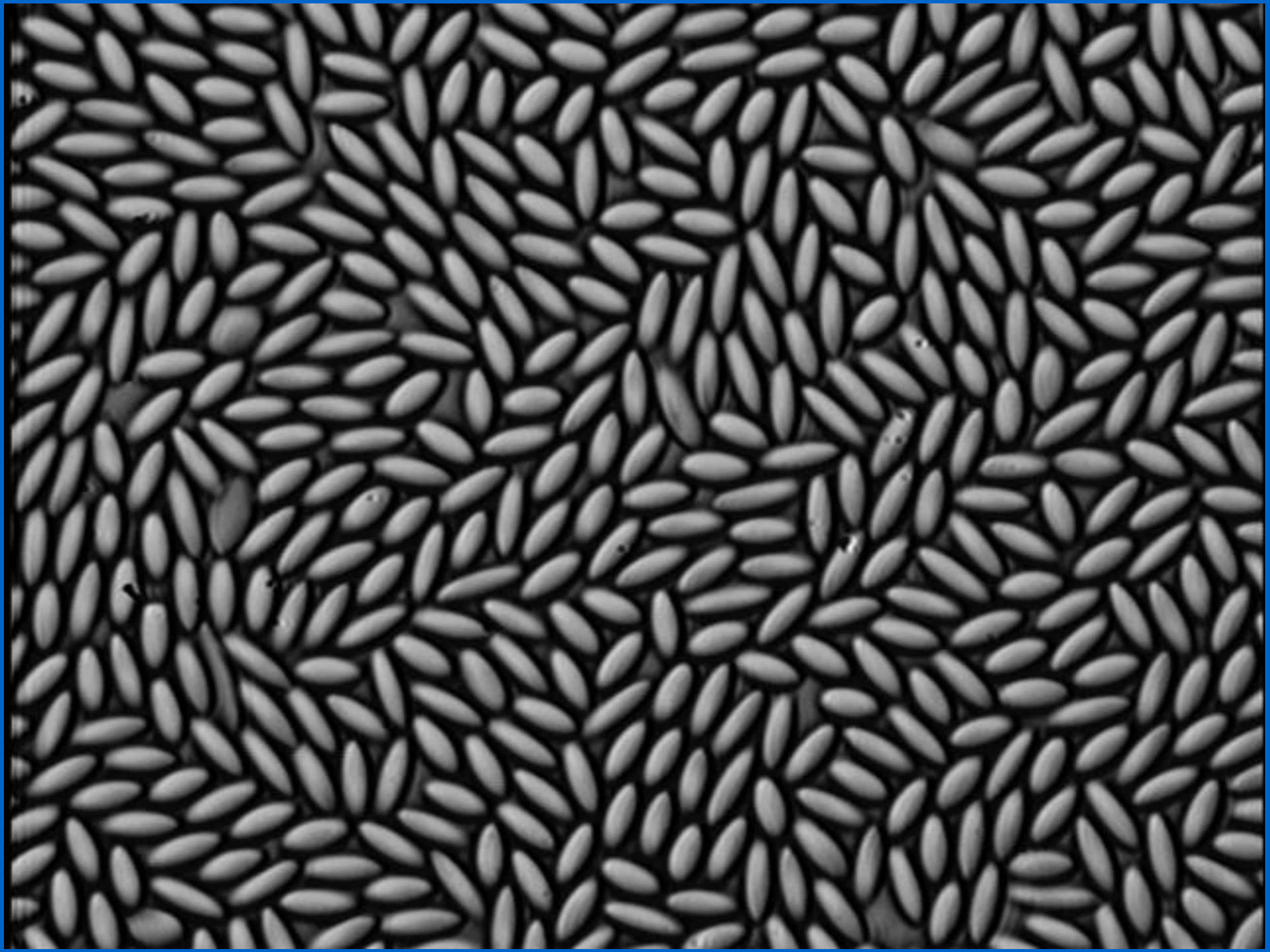
Cubatic Phase Identified by g_4



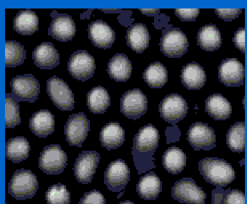
$$\Psi_{\alpha j} = \sum_{k=1}^{NN} e^{i\alpha\theta_{jk}}$$

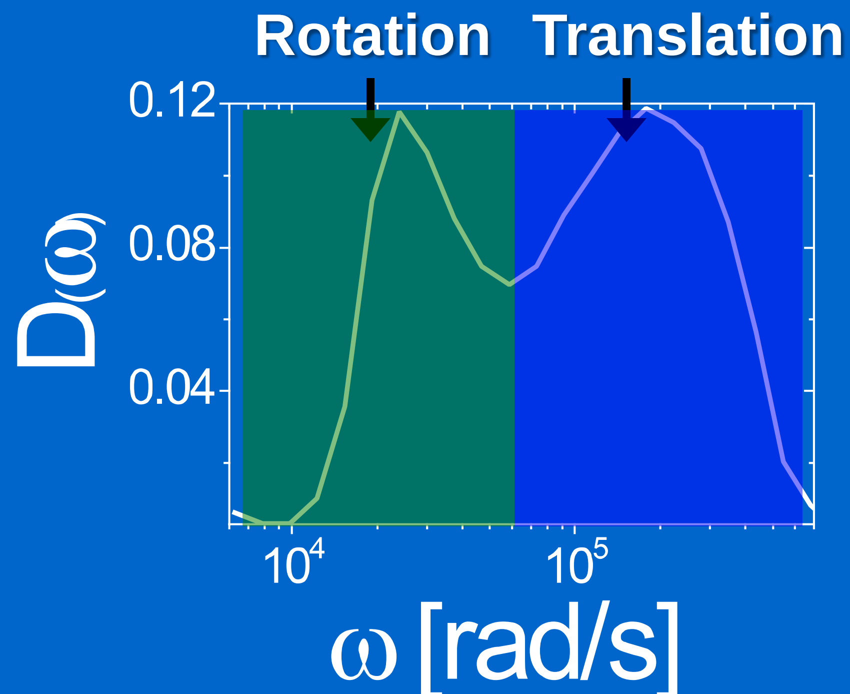
$$g_{\alpha}(r) = \left\langle \Psi^{*}_{\alpha k}(r_k)\Psi_{\alpha j}(r_j) \right\rangle$$

Ellipsoids

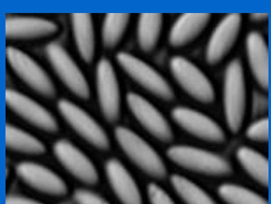


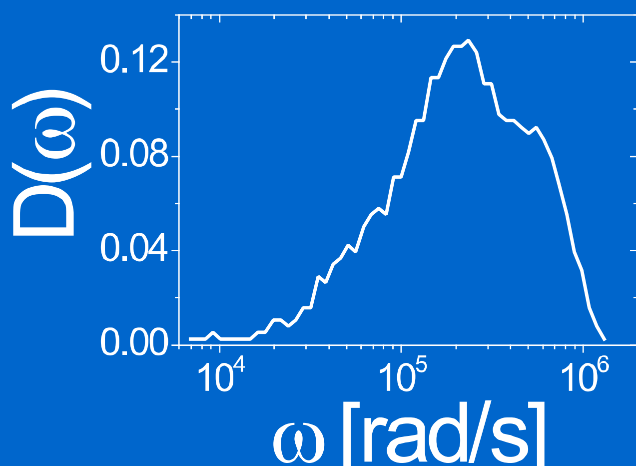
Glasses composed of Ellipsoids: Phonons





Translation-Rotation Coupling Depends on Aspect Ratio



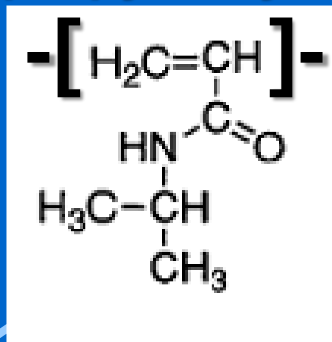


Yunker, P.J., Chen, K., Zhang, Z.X., Ellenbroek, W.G., Liu, A.J., and Yodh, A.G., Rotational and translational phonon modes in glasses composed of ellipsoidal particles. *Physical Review* E 83, 011403 (2011).

NIPA Particles

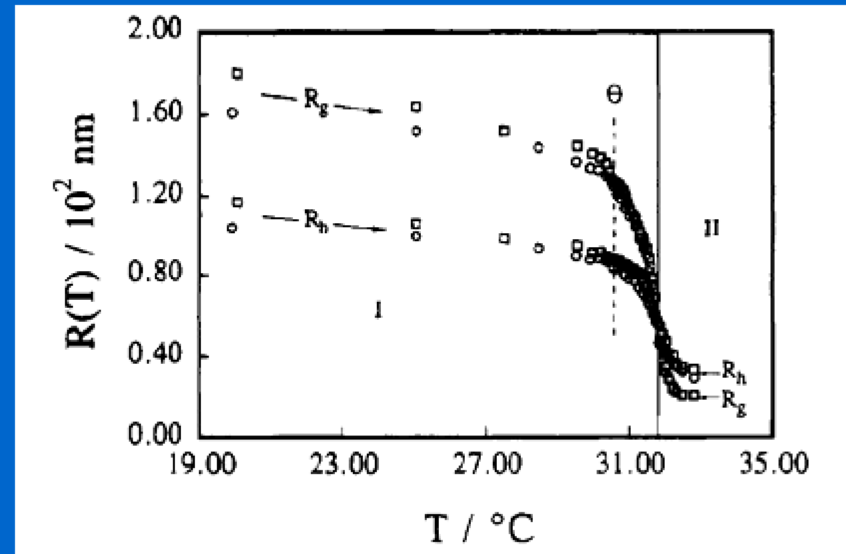
Temperature-Sensitive NIPA Polymer

N-isopropyl acrylamide

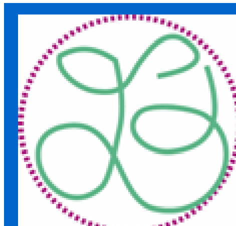


acrylamide group (hydrophilic)

Propyl group (hydrophobic)



M_w~250k



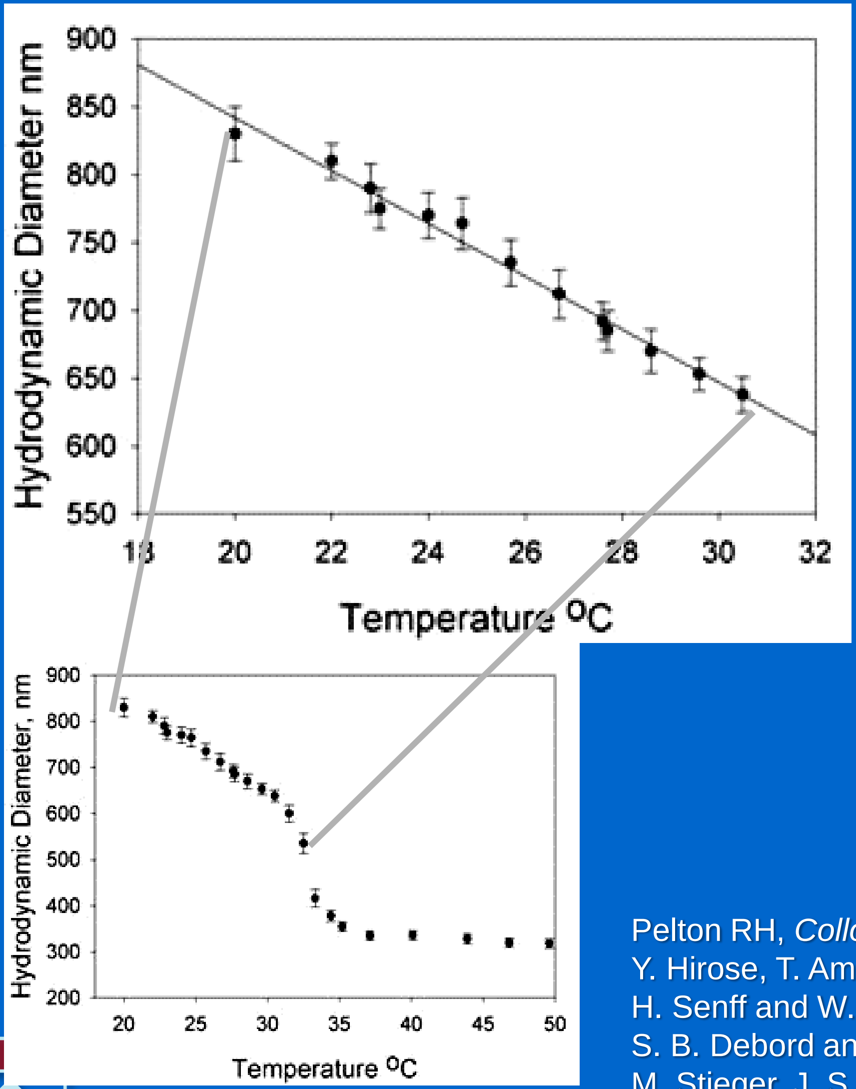
Increasing temp

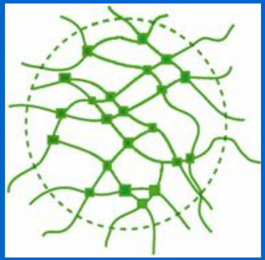
~32^{o}C

at 10^{o}C C^*~ 0.01 gm/ml R_g~ 55 nm

M. Heskins, J. E. Guillet, Journal of Macromolecular Science, Part A, V.2, Issue 8, (1968).
Charles I. Chiklis, J. Michael Grasshoff, Journal of Polymer Science, Part A-2, V. 8, (1970).
Eriko Sato Matsuo & Toyoichi Tanaka, Nature, 325 (1987).
C. Wu and X. Wang, Phys. Rev. Lett. 80, (1998)

NIPA Microgel Spherical Particles

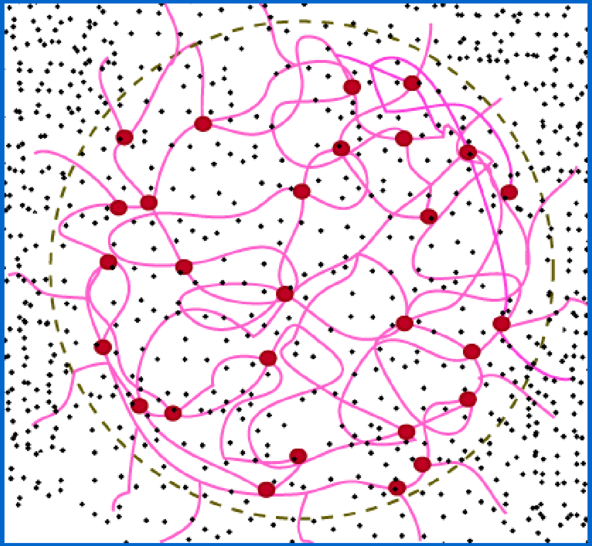




Increase Temperature

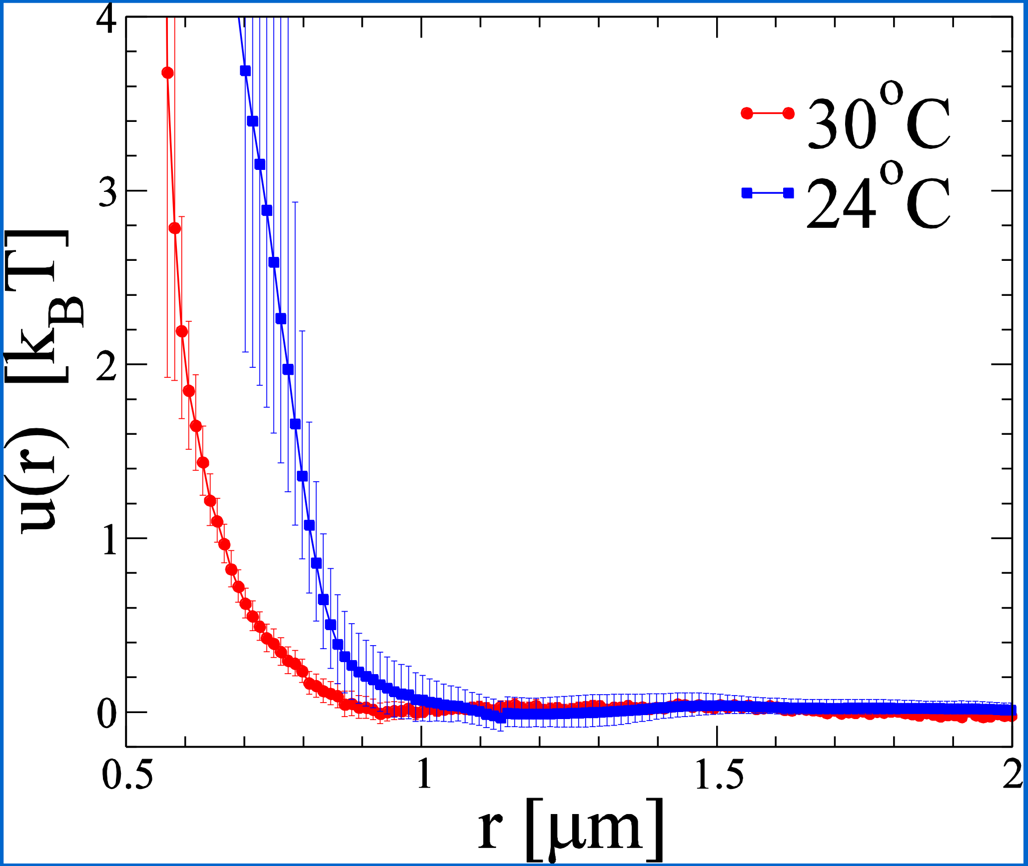
Water flows out

~ 4% polymer , ~96% water



Pelton RH, *Colloids & Surfaces*, V. 20, Issue: 3 (1986).
Y. Hirose, T. Amiya, Y. Hirokawa & T. Tanaka, *Macromolecules*, V. 20, (1987).
H. Senff and W. Richtering, *Journal of Chemical Physics,* 111, (1999)
S. B. Debord and L. A. Lyon, *J. Phys. Chem. B* 107 (2003)
M. Stieger, J. S. Pedersen, P. Lindner, W. Richtering, *Langmuir* 20, (2004)

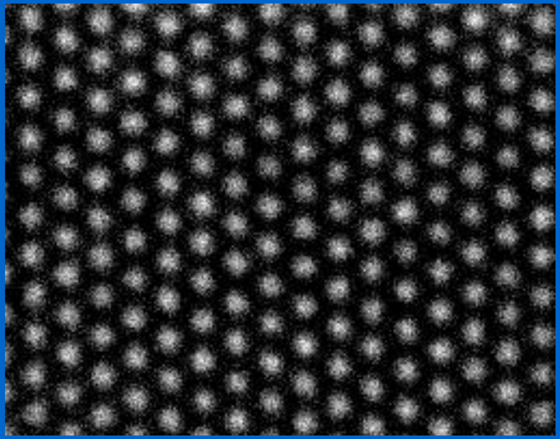
Interparticle Potentials from g(r) in the Dilute Limit



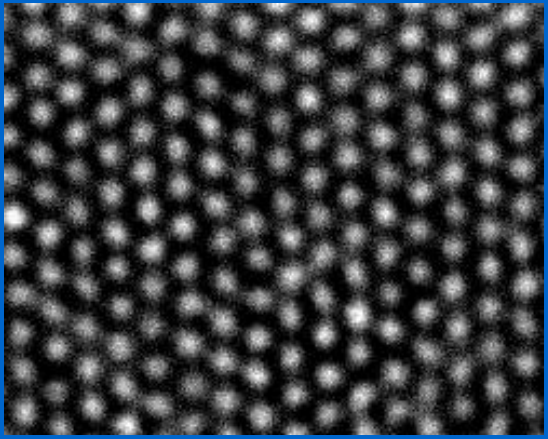
Repulsive Short-range (relatively soft) 'Central Force'

Han, Y., Ha, N.Y., Alsayed, A.M., and Yodh, A.G., *PRE* 77, (2008); Zhang, Z., Xu, N., Chen, D.T.N., Yunker, P., Alsayed, A., Aptowicz, K.B., Habdas, P., Liu, A.J., Nagel, S., Yodh, A.G., *Nature* 459, (2009)

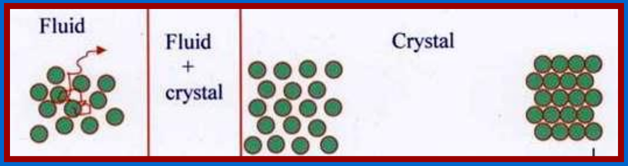
Easy to Change Volume Fraction



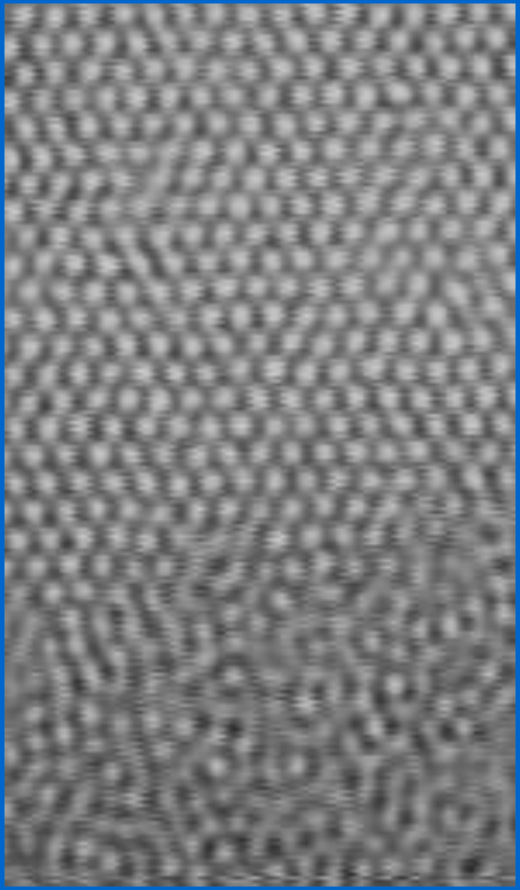
T = 23 ºC , ϕ ~ 0.830



T = 27.9 ºC, ϕ ~ 0.580



increase T, decrease ϕ

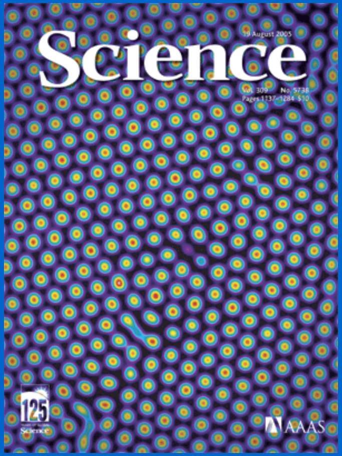


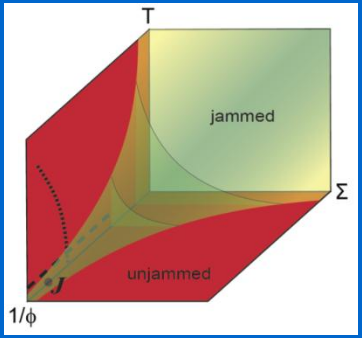
T = 28.3 ºC, ϕ ~ 0.547

- "Knob" to Control Phase Behavior, Effective Interactions
- Permits Visualization of Samples Transforming from One Phase to Another

Swellable Particles are Swell

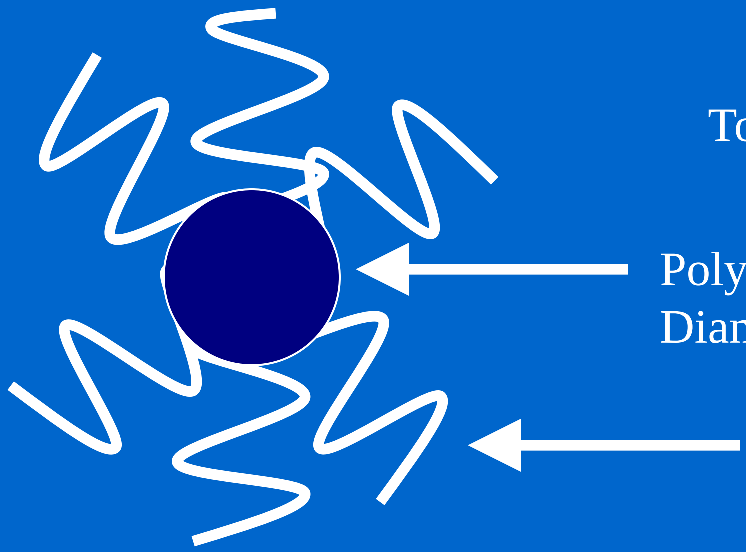
- Melting in 3D, 2D, Thin Films, & quasi-1D (cylinders) (Science, 2005; PRE, 2008; PRL, 2010; PRE, 2010)
- Freezing Criteria in 2D (JCP, 2010)
- Colloidal Antiferromagnets (Nature, 2008)
- Aging in Glasses (PRL, 2009)
- Crystal-Glass Transition (PRL, 2010)





- Jamming: Structural Signatures (Nature, 2009)
- Jamming: Shadow Systems, Phonon Density of States (PRL, 2010)

Core-Shell PS/PMMA/Silica-PNIPAm Colloids



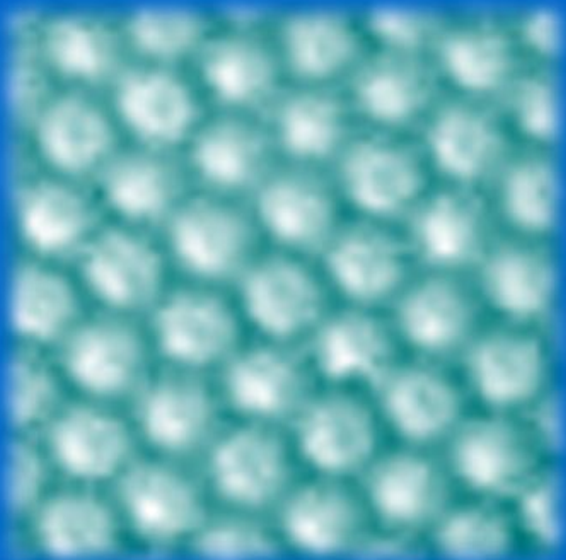
Background Fluid: Cargille Immersion Liquid

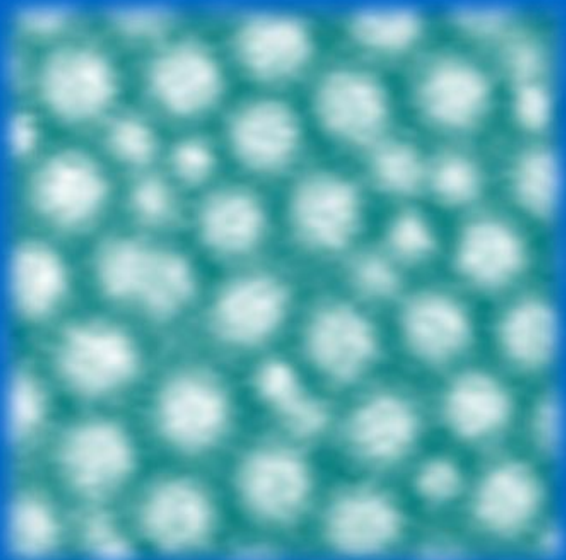
•Refractive index matched with polystyrene

•Density of fluid ~twice density of PS!

(Cargille Immersion Liquid Code OHZB, *n* = 1.556 at 25° C)

Disorder-induced Crystal-Glass Transition

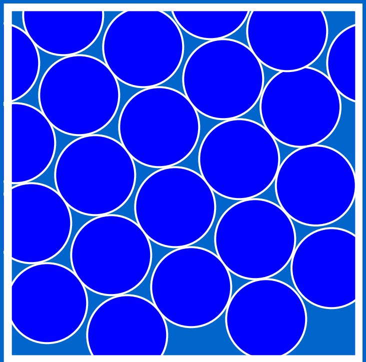




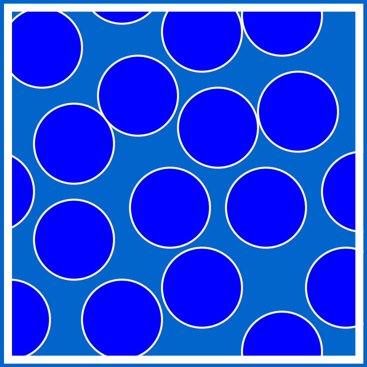
Yunker, P., Zhang, Z.X., and Yodh, A.G., Observation of the disorder-induced crystal-to-glass transition. *Physical Review Letters* 104, 015701 (2010).

Crystal-to-liquid transition is sharp

- Orientational order ↓
- Correlation length ↓ (long-range to short-range)
- Susceptibilities peak at transition

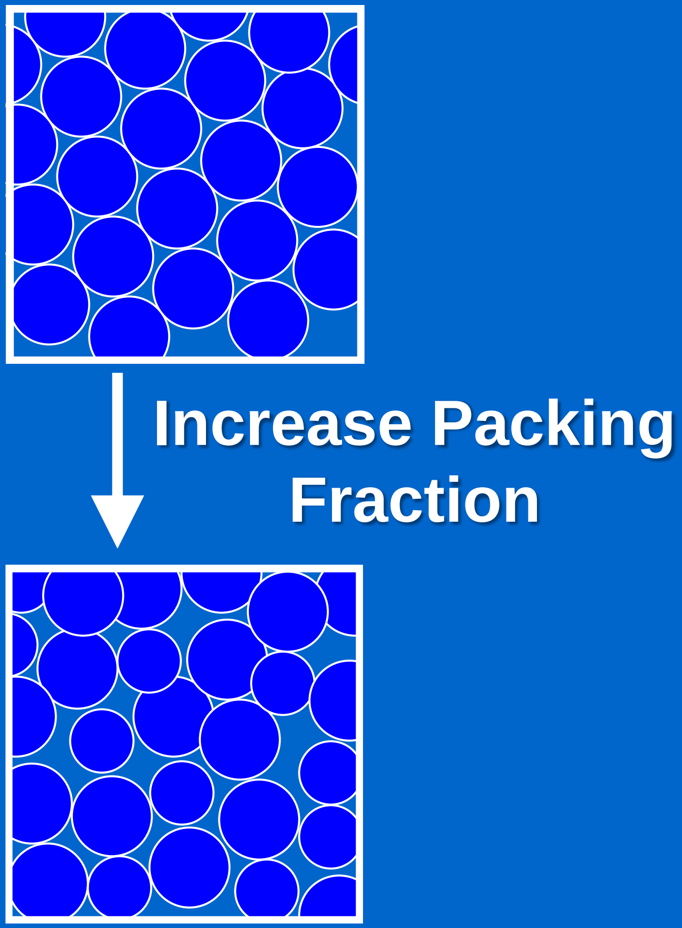


Small decrease in packing fraction



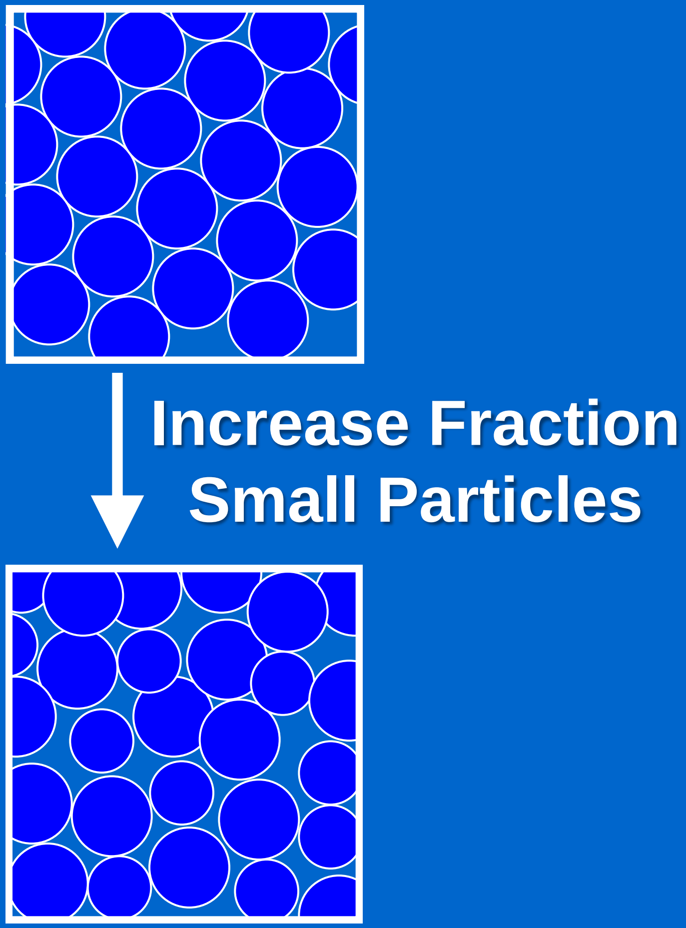
Liquid to Glass Transition is not as Sharp as Liquid to Crystal

- **Relaxation time ↑**
- **Structural correlations ~same**
- **Correlated rearrangements**



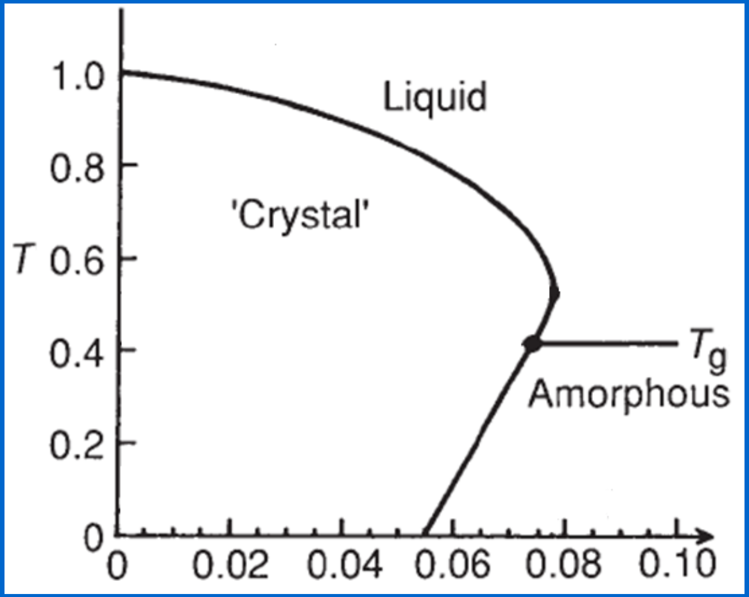
Crystal to Glass Transition is different from both

- φ ~constant
- Relaxation time ~constant
- Decrease in structural correlations
- Dynamic heterogeneity

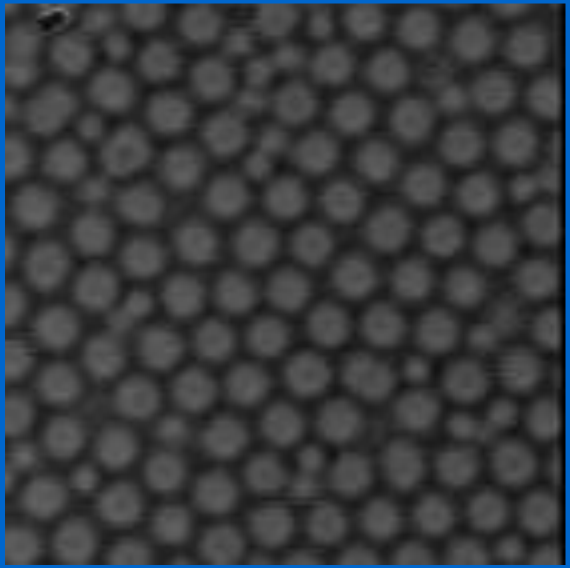


Theories Predict 'Phase Transition' from Crystal to Glass

Crystal



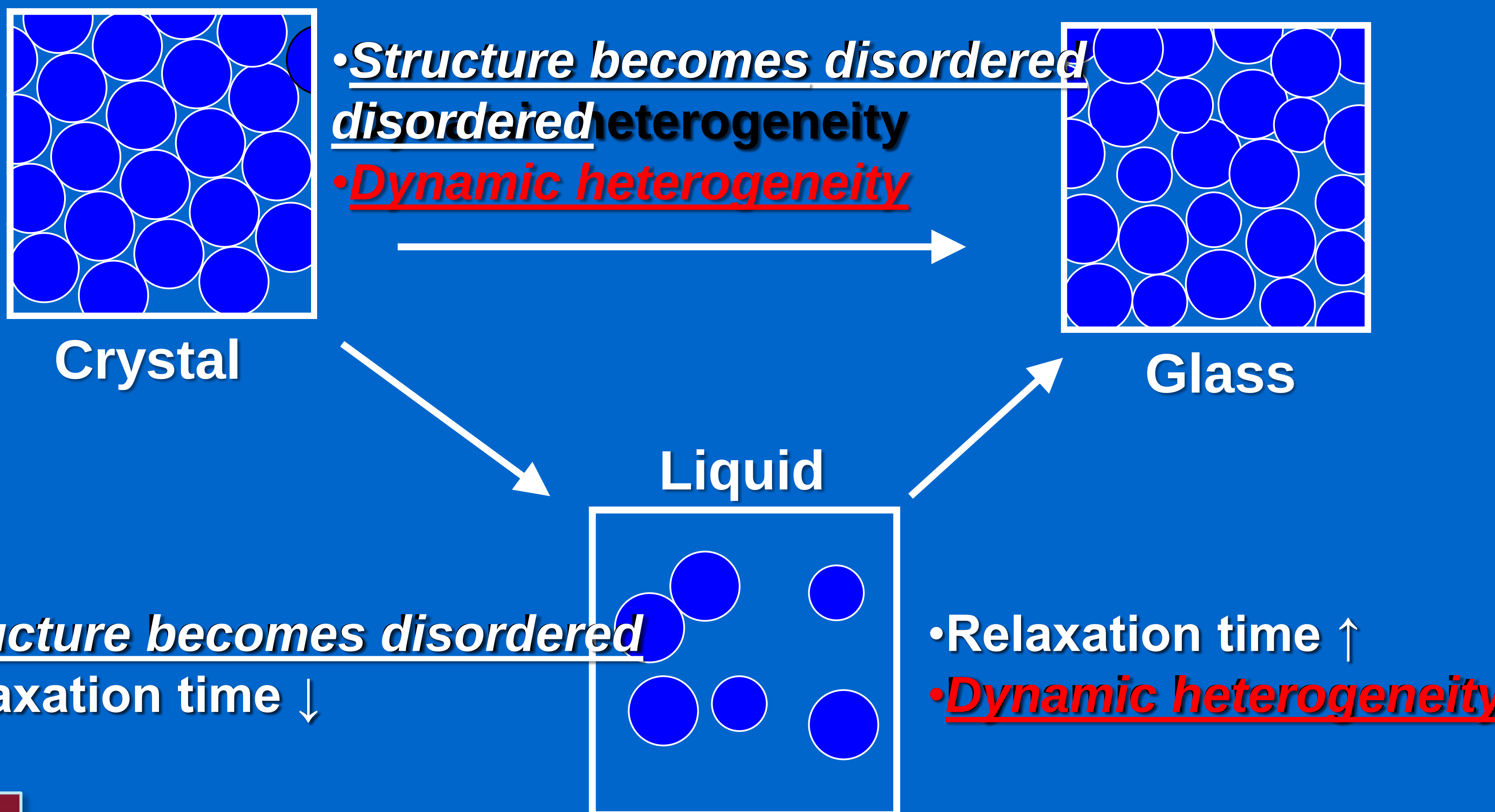
Quenched Disorder



Glass

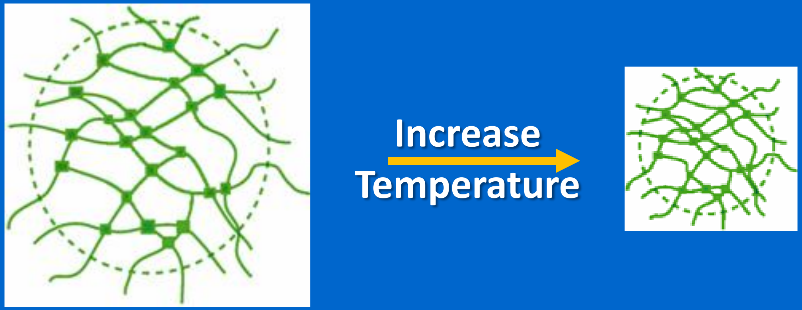
Nelson PRE (1983), Fecht Nature (1992), Li PRB (2000), Onukie PRE (2007)

Does dynamic heterogeneity “turn on” when disorder “turns on”?

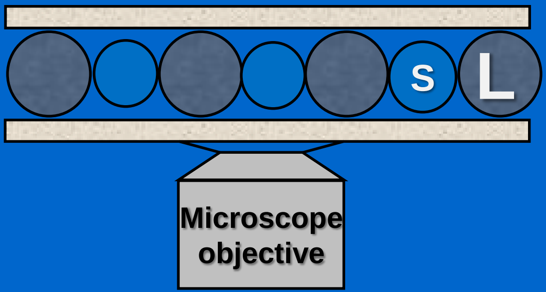


Experiment (2D)

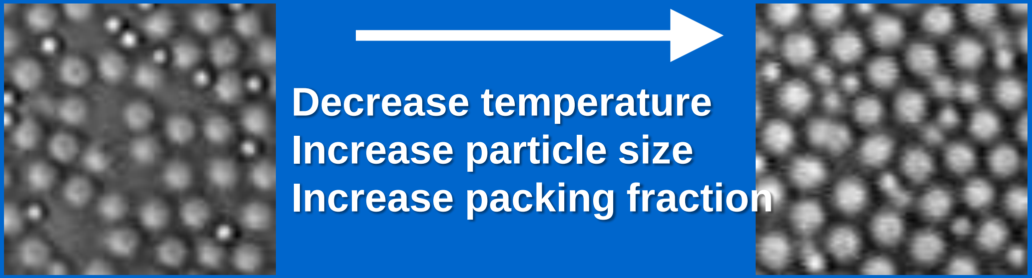
- **N-isopropylacrylamide (NIPA) microspheres**



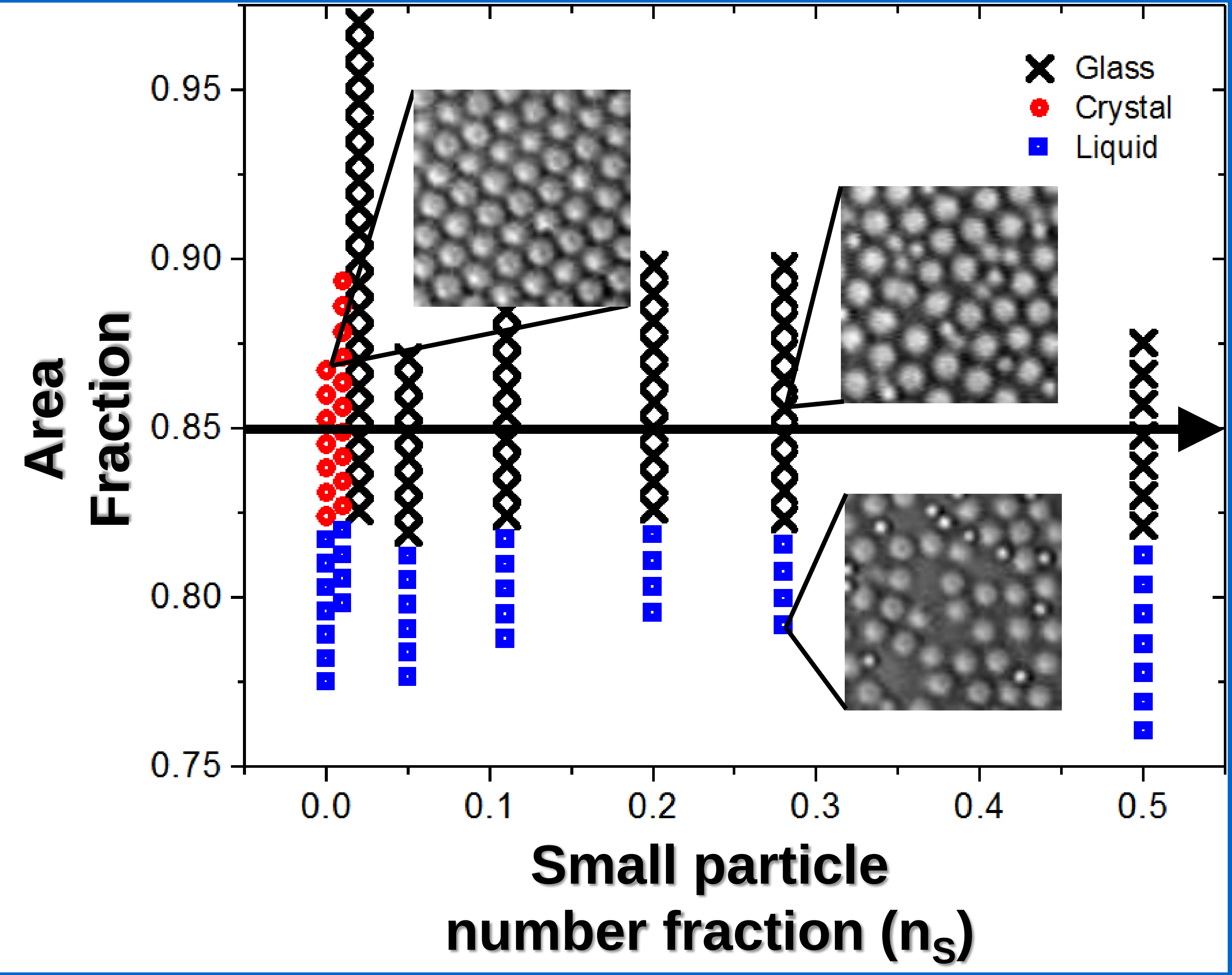
- **Confine to quasi-2D chamber**



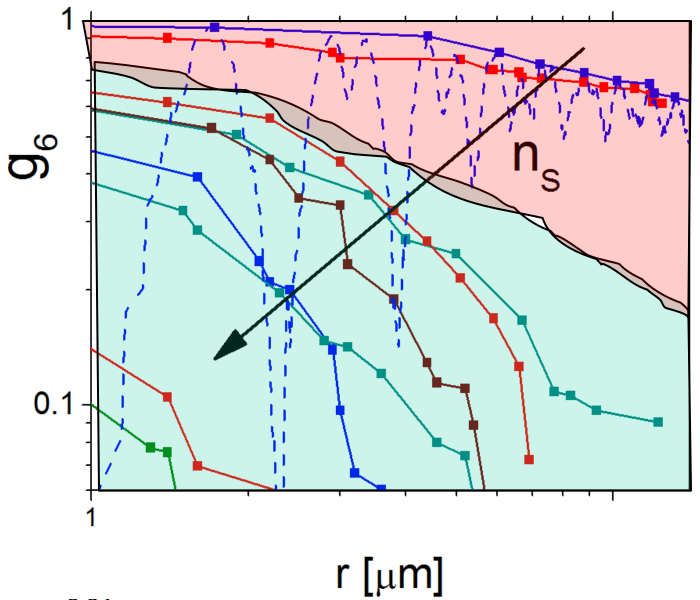
- **Bidisperse: Large & Small NIPA particles**
- **Size ratio =1.33 (D_L = 1.6 μm, D_s= 1.2 μm)**

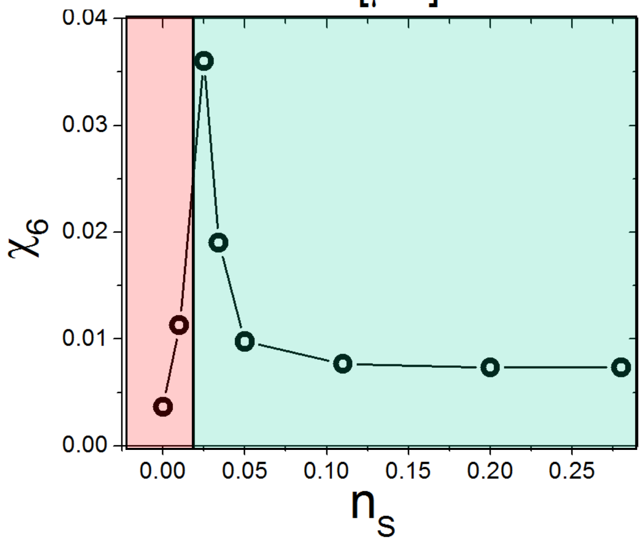


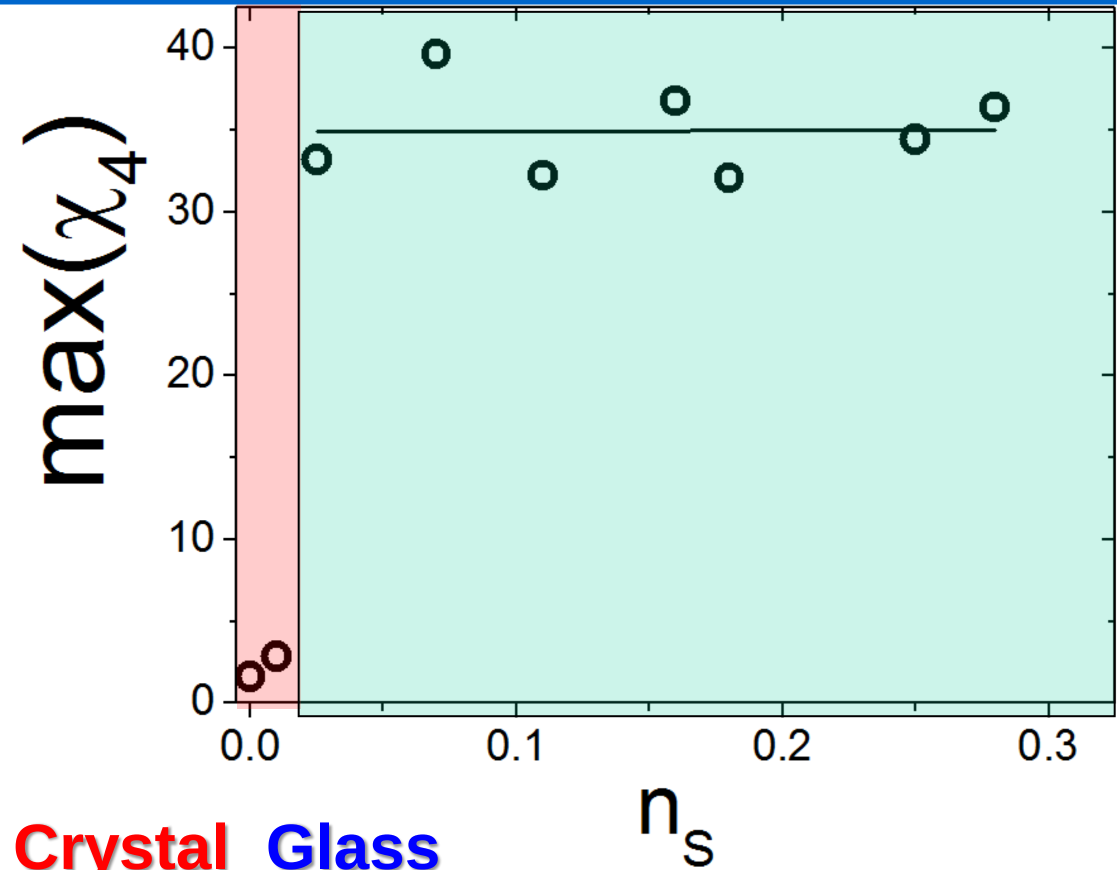
Quenched Disorder Phase Diagram



Dynamic and Structural Transitions Coincide







Crystal **Glass**

Area Fraction = 0.85

Crystal-to-Glass Summary

- **Glass can be understood in the context of *Order-to-Disorder* transitions**
  - Structural correlations disappear abruptly
  - Correlated rearrangements *turn on* when long-range order disappears

P. Yunker, Z. Zhang, A. G. Yodh, PRL (2010)

WHAT HAPPENS IN 3D?

- Nature of Liquid-Crystal Transition is different than 2D.
- Nature of Liquid-Glass Transition is expected to be similar to 2D.
- Coexistence
- Problem is much richer than in 2D.

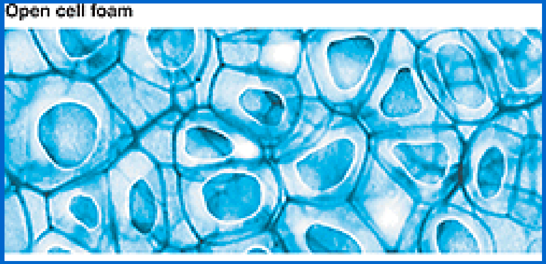
Plans

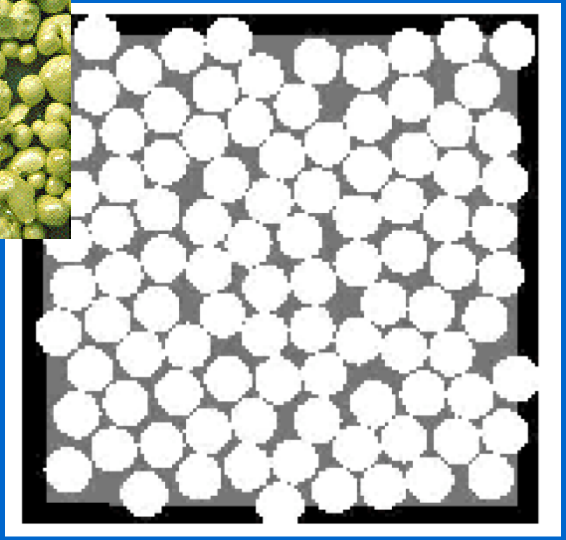
- Without temperature-sensitivity (Ace-1A), use index-matched particles to map basic effects.
- With temperature-sensitivity (Ace-1B), use index-matched core-shell PS/PMMA-NIPA particles to much more fully map basic effects.
- Microscopy can be used to measure same parameters in image slices.

Why microgravity?

- With temperature-sensitive particles, cannot simultaneously index- and density-match.
- With index matching, can look far into 3D samples (i.e., far from wall effects).
- Sedimentation effects can be important for segregation, especially during coexistence. Gravity affects crystallization.

Jamming: Motion stopped or clogged

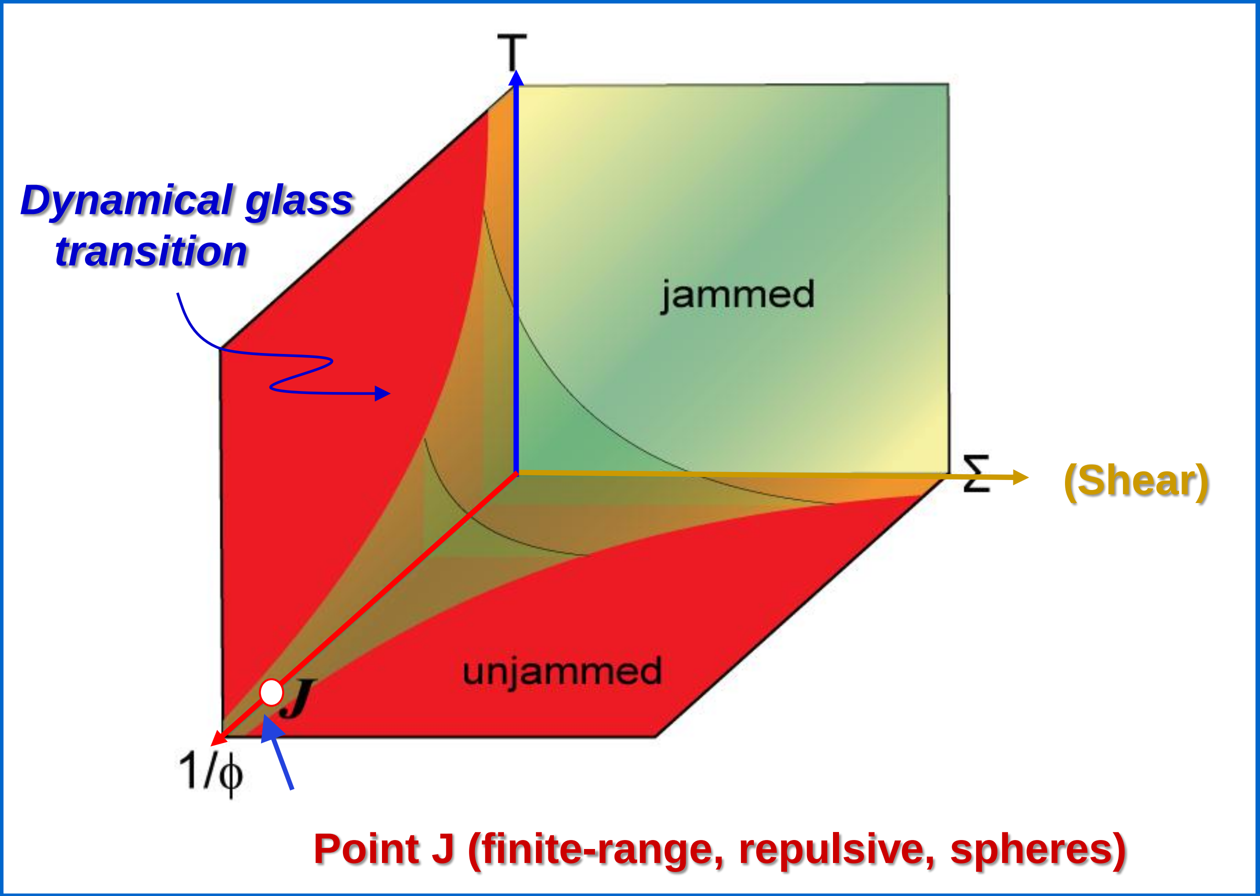




- Disordered medium ‘stuck’ in phase space

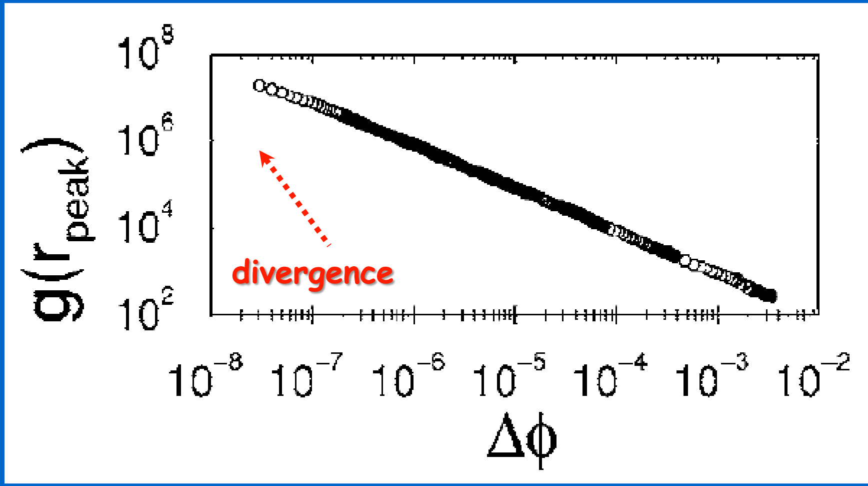
Jamming Phase Diagram

Liu, A. J. & Nagel, S. R., Nature 396, 21-22 (1998)



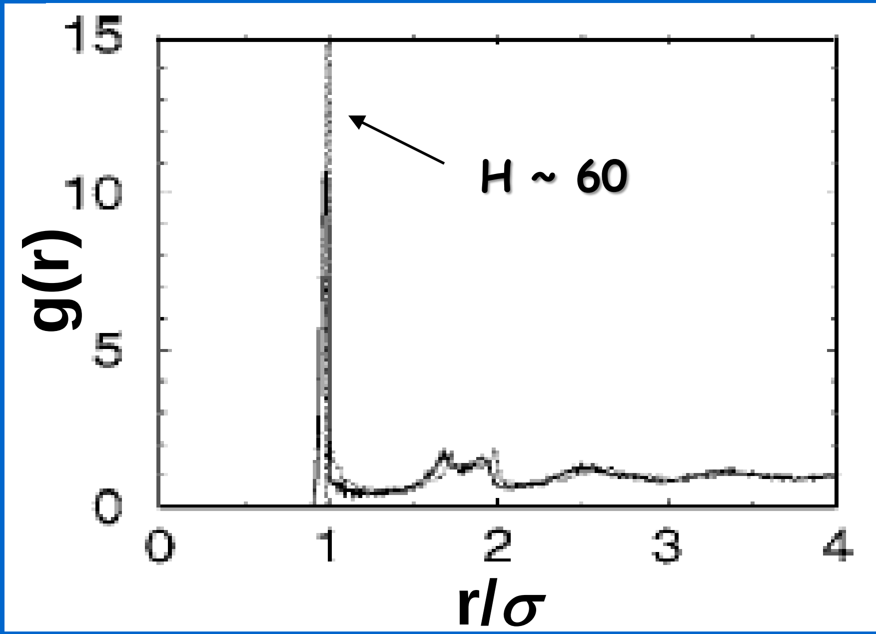
- Point-J is a unique point
- Mixed-order phase transition; multiple length scales divergence…

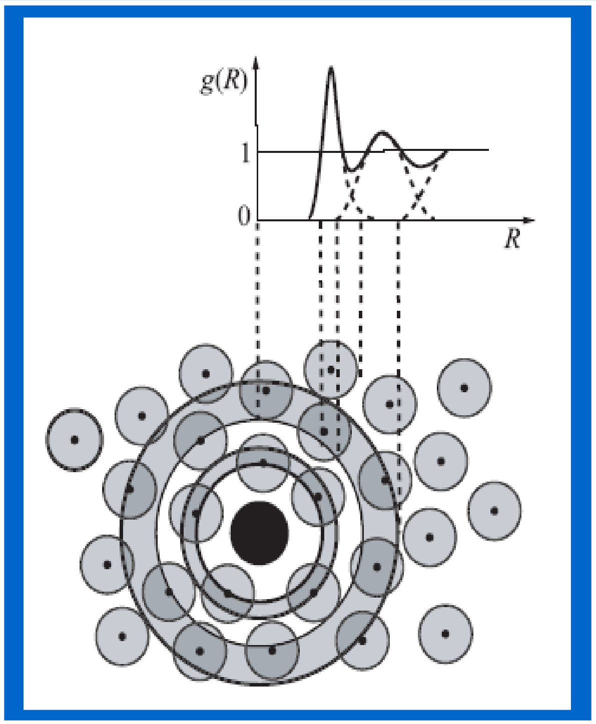
Structural Signature at Point J



- 1st peak of g(r) diverge at r= σ at *Δφ~ 0*

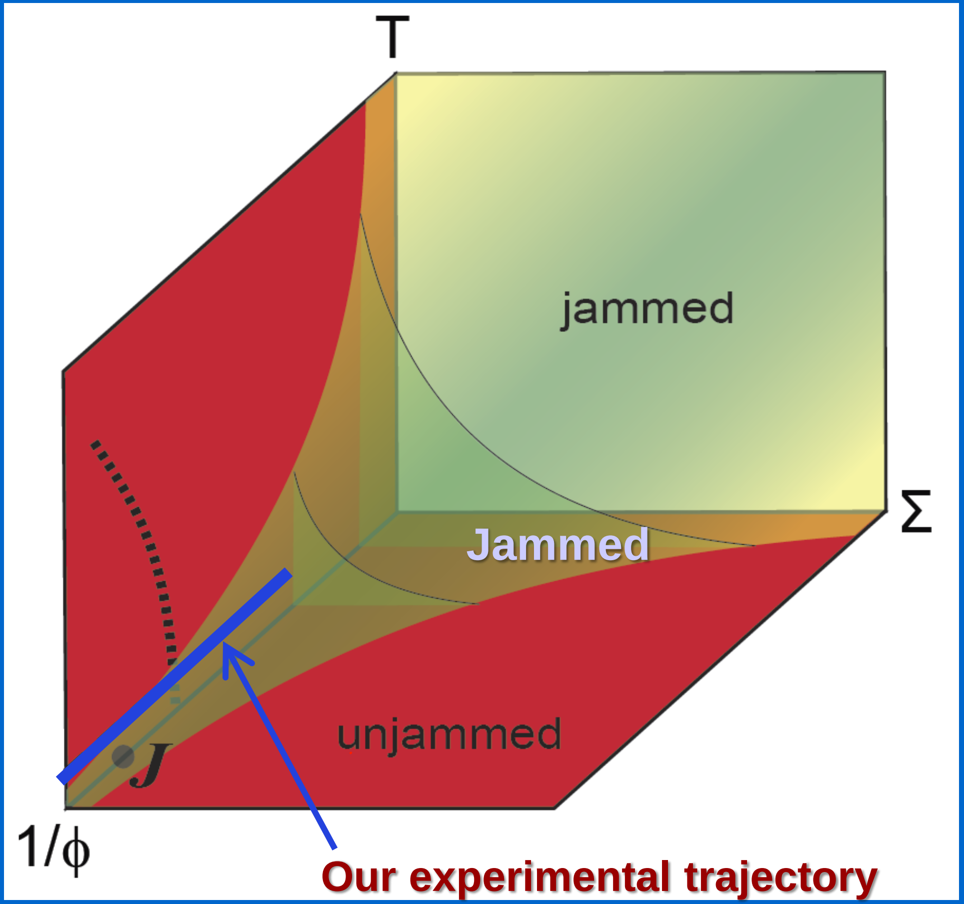
(O'Hern, Silbert, Liu, Nagel, PRE 68, 2003)



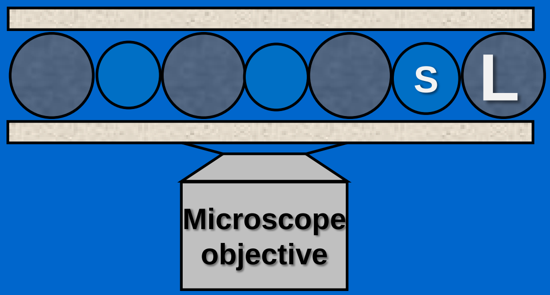


schematic of g(r)

Colloidal Jamming



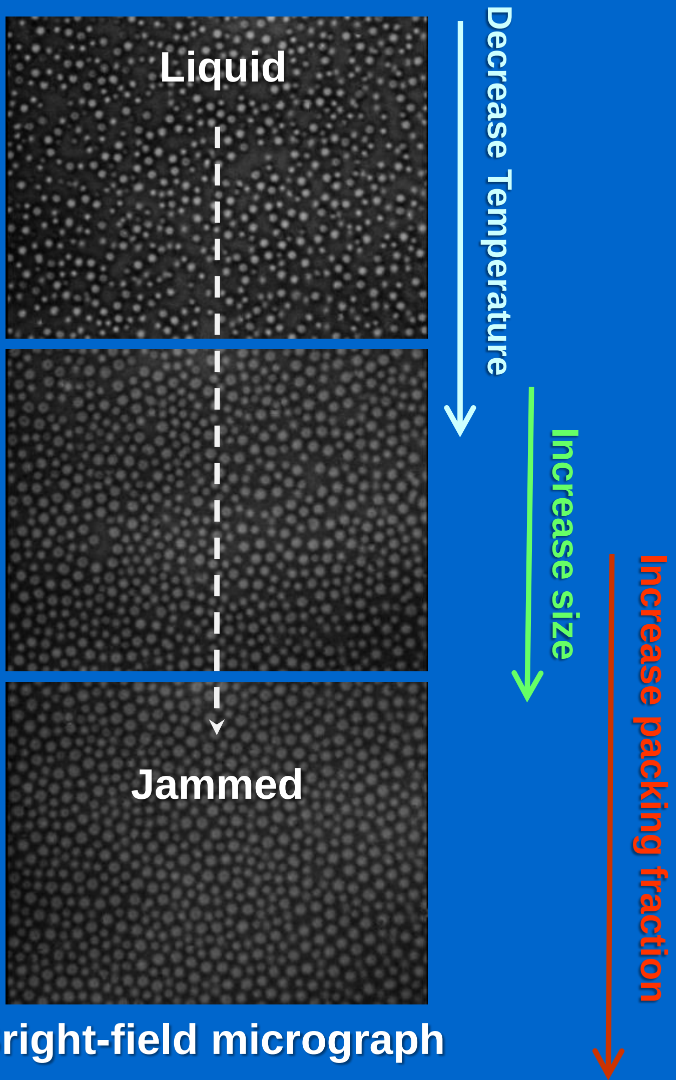
2D Setup for Jamming Experiment



- Bidisperse: Large & Small NIPA particles
- 1:1 mixture (by number)
- Size ratio =1.33 (D_L = 1.6 μm, D_s= 1.2 μm)

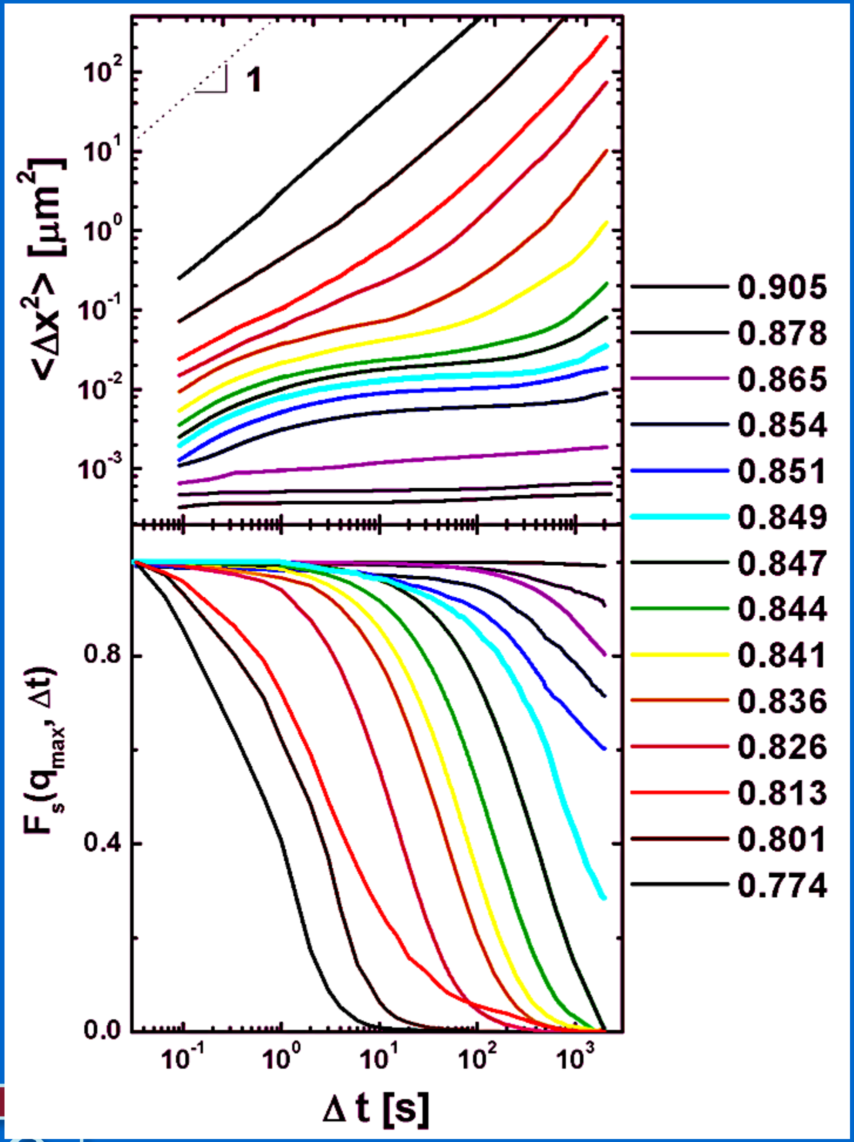
Digital Microscopy

- Camera speed: 30 frames/sec
- 1 hour of video at each temperature
- Field of view: 80 × 60 μm², N ~ 3000 particles
- Particle tracking
- Dynamic and structural features



Bright-field micrograph

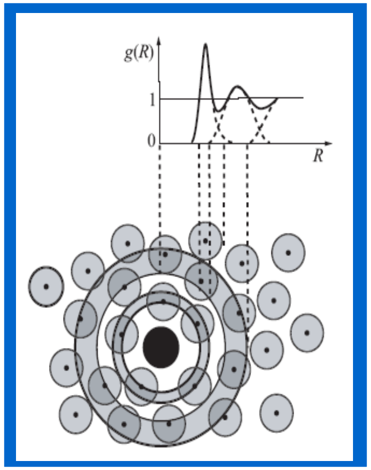
Glassy Dynamics as expected



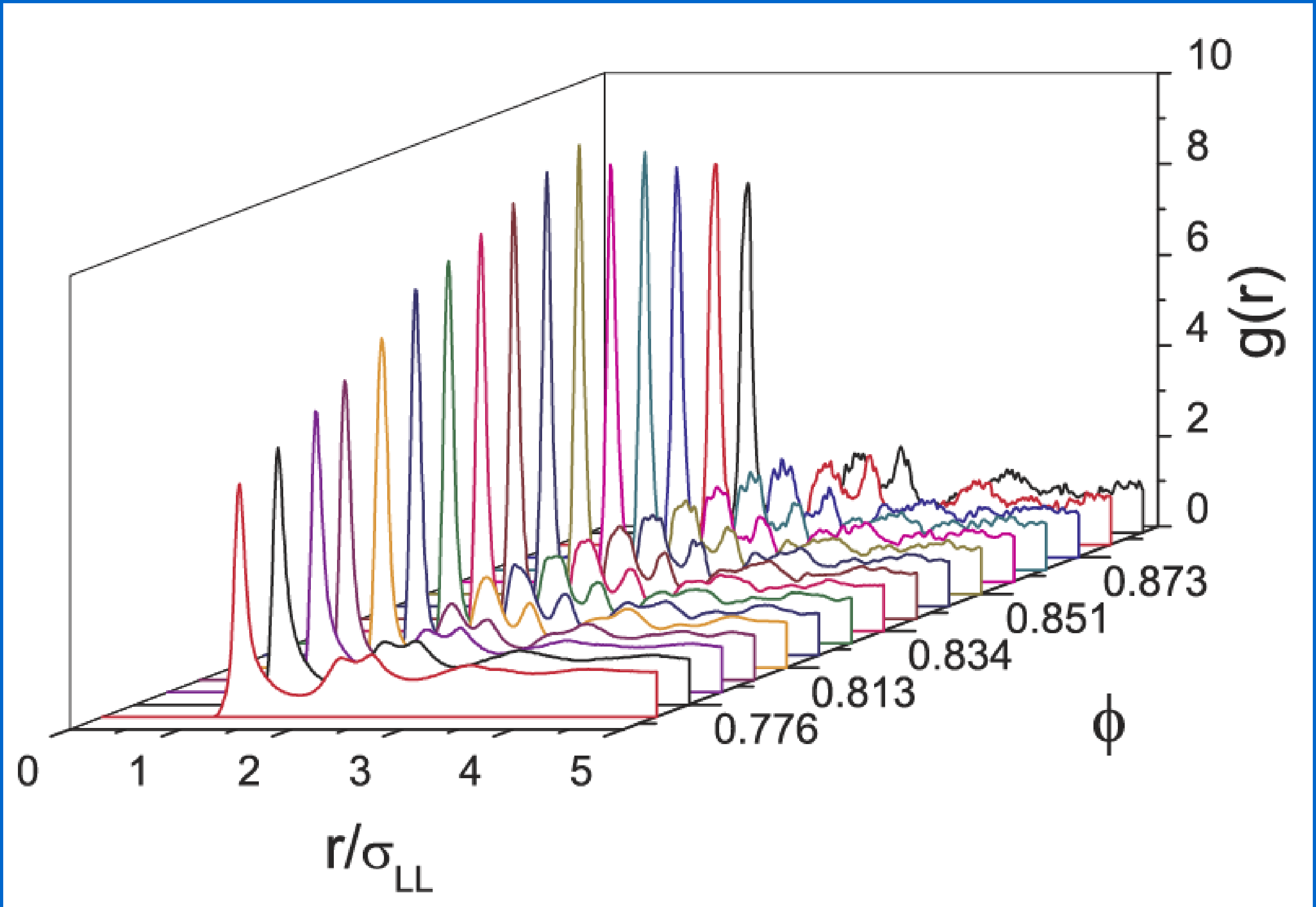
$<\Delta x^2> = <[x(t) - x(0)]^2>$,

$F_s(q,t) \sim (1/N)\{\Sigma_i \exp(iq \cdot [r_i(t) - r_i(0)])\}$

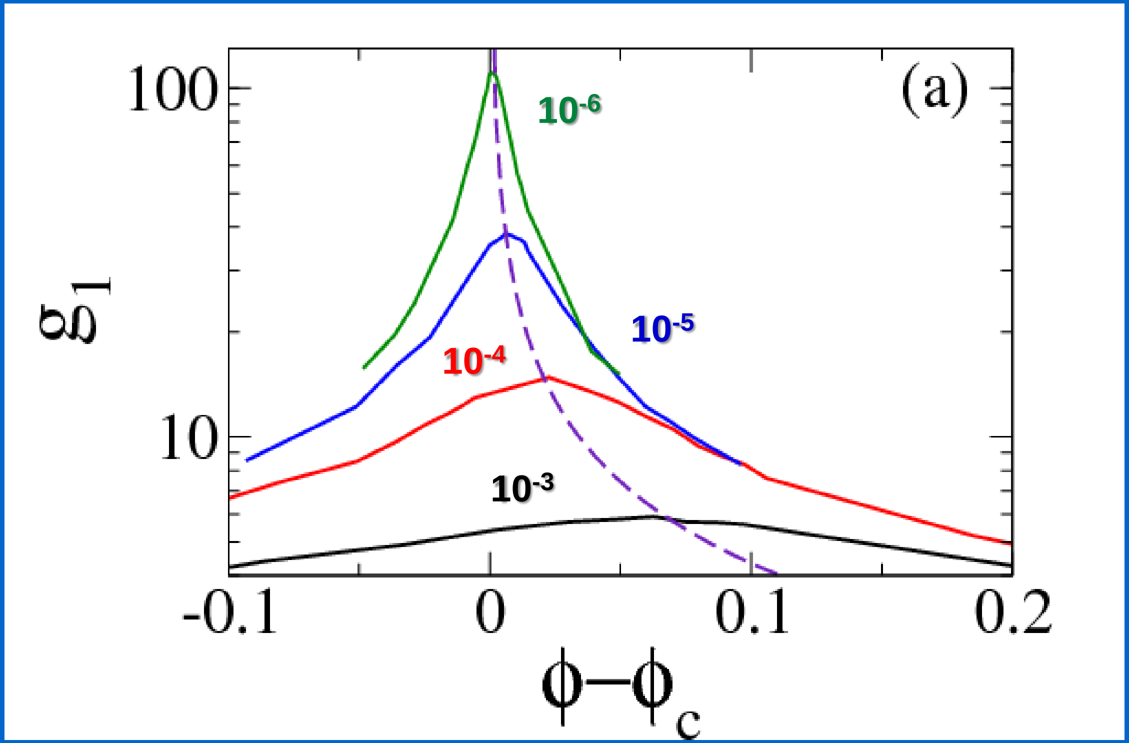
Structure Signature: Pair Correlation Function

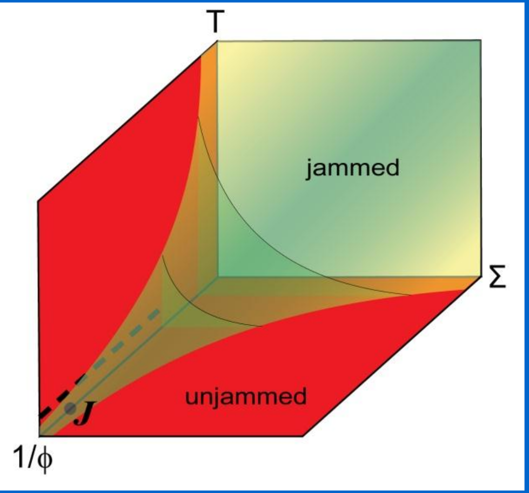


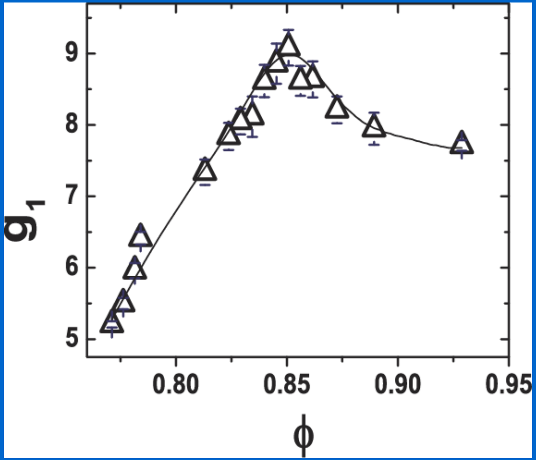
schematic of g(r)



Simulation: Maxima in g(r) at Finite Temperature







Simulation:
Fix temperature, changing volume fraction
Same route as experiment

- **Structural signature, the g_1 maxima, also evident when changing packing fraction (pressure) at fixed temperature**
- **Simulations are consistent result for experiments**

Jamming Summary

- **Structural and Dynamical Signatures of the jamming transition observed in 2D.**

What happens in 3D Jamming?

- Coordination is different, but excess coordination (above rigidity onset / jamming transition) should behave the same.

Plans

- Without temperature-sensitivity (Ace-1A), use index-matched (core-shell/soft) particles at various volume fractions to map basic effects (dynamical and structural).
- With temperature-sensitivity (Ace-1B), use index-matched core-shell PS/PMMA-NIPA particles to much more fully map basic effects.
- Microscopy can be used to measure same parameters in image slices.

Why microgravity?

- With temperature-sensitive particles, cannot simultaneously index- and density-match.
- With index matching, can look far into 3D samples (i.e., far from wall effects).
- Sedimentation effects can smear out g(r), even for very small effects. The peak in g(r) is a small effect.

OTHER EXPERIMENTS

- Ellipsoid Jamming (packings jam even if not isostatic). 3D, confocal (Ace-2/3).
- Lyotropic LCs, melting behaviors
- Colloidal Droplets, crystallization behaviors

Microgravity Justification (as before)

- Formation of colloidal crystals is profoundly affected by gravity via sedimentation processes. Chaikin and Russel have already demonstrated this effect in space experiments exploring the simplest of all entropic transitions, the hard-sphere liquid-solid phase transition.
- Sedimentation causes particles to fall so rapidly that there is insufficient time for particles to explore the full phase space of positions and velocities that are required for thermodynamic assembly processes. A substantial particle concentration gradient arises in the earthbound sample.

$$h = \frac{kT}{\Delta\rho V g}$$

h= gravitational height
kT = Thermal Energy of system
$\Delta\rho$ is the density difference between the particles and the background fluid
V is the particle volume
g is the gravitational acceleration

h ranges from a few microns for the case of polystyrene in water to a fraction of a micron for most of the other particles we consider. Our particles are usually of order 1 micron in diameter.

Microgravity Justification

continued

- In addition, the shear forces of fluid flow due to the sedimenting particles is often sufficient to break crystals that are forming thermodynamically.
- The solvents we plan to use (preferably water) are restricted by various factors, for example by our need to fix the colloidal structures in space. Almost all of the particles of future interest are either too heavy or too light compared to water.
- Sample equilibration often requires ~1 to 12 hours. Crystal growth sometimes continues for one to two more weeks after the initiation process. These processes are too slow for a drop tower or an airplane.
- Space station or space shuttle provides an environment where microgravity is sustained long enough to allow these experiments to be conducted. The samples can be homogenized, and then allowed to develop in the microgravity environment. Their structures and optical properties can be measured. For most samples we are contemplating, the density mismatch between particle and background fluid is large (e.g. >1.1x). Microgravity dramatically reduces these differences and permits true equilibrium processes to occur.

Experimental Concept

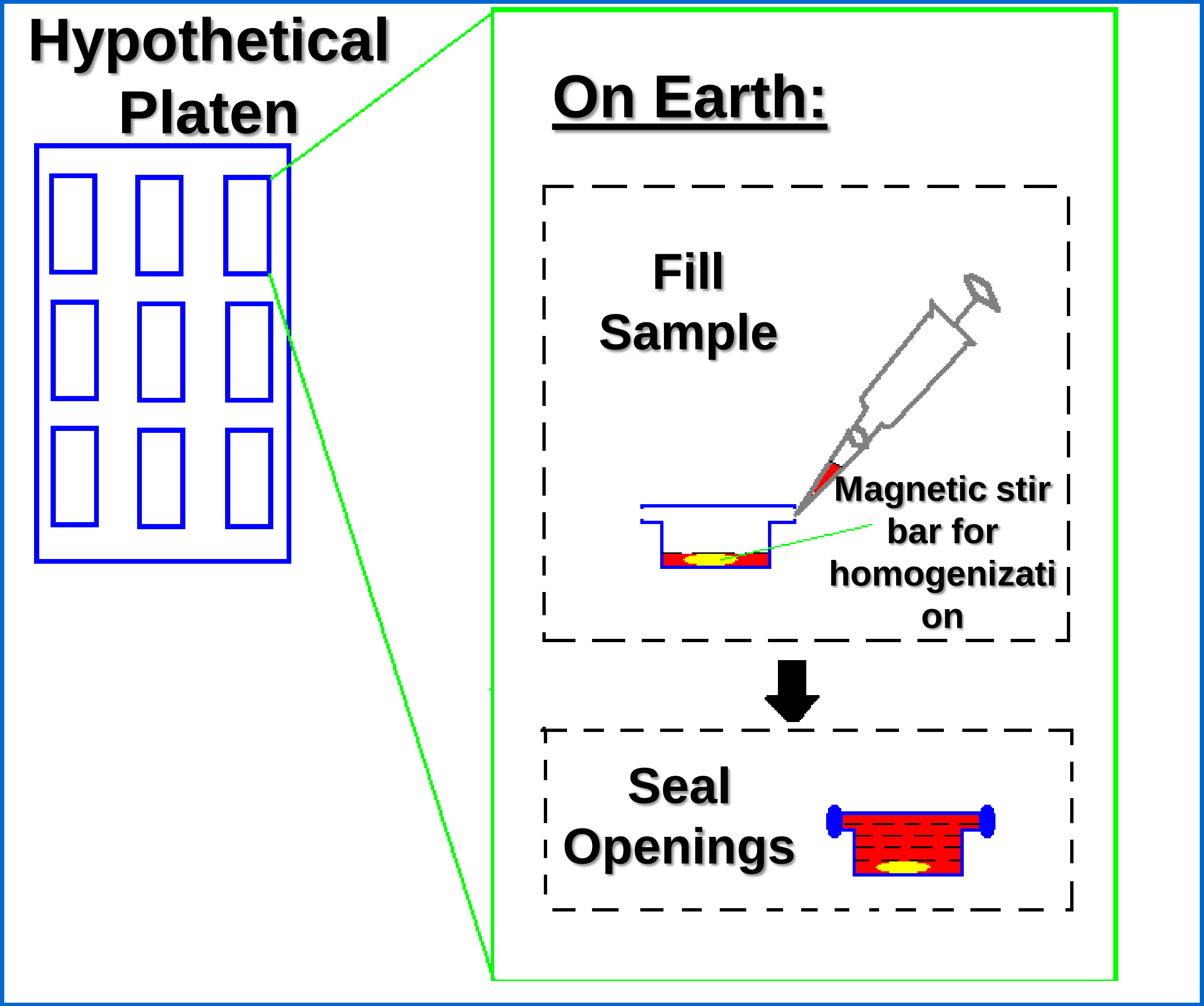
The following lists the techniques necessary for sample handling and the experiments.

1. **Sample Creation and Variation** – The principle samples we will study will consist of colloidal particles in a suspending background fluid such as water. Controlled variation of particle type will be carried out in order to study phase behavior, etc. These suspensions will be injected into the sample cells prior to or during flight.

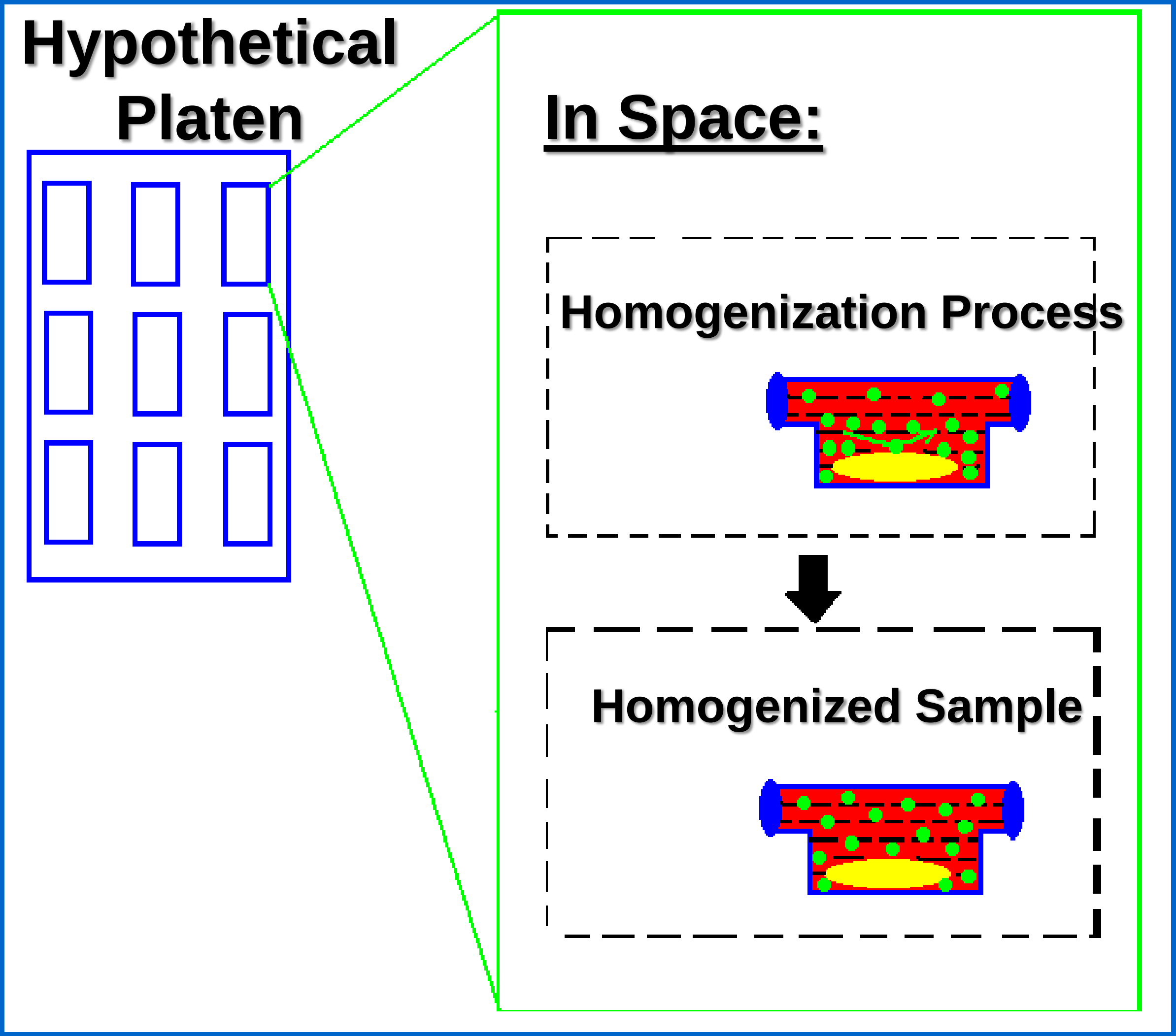
2. **Sample Homogenization** – Shear melting/mixing using micro-stirrers allows for the dissolution of the crystallites/aggregates that have formed in 1g before launch or have formed prior to experimentation during flight. It defines a starting time for crystallites to begin forming. All NIPA based samples can be homogenized with temperature variation.

3. **Microscopy (Real Space)** - One goal of this experiment is the microscopic observation of colloidal structure and dynamics. Sample observation after mixing will confirm homogenization of the samples. Then we will employ microscopy to observe sample morphology after equilibration, as function of sample temperature, etc. To the best of our ability we will determine phases that form, and the structural/dynamical properties of these phases.

Sample handling



Sample handling



Science Requirements

PRIMARY IN-FLIGHT TASKS

- **HOMOGENIZATION**

Shear melting/mixing allows for the dissolution of the crystallites/aggregates that have formed in 1g before launch or have formed prior to experimentation during flight.

Defines a starting time for sample evolution (recorded within a few minutes of the actual start-time).

Microscopic observation in a few selected samples is desirable in order to confirm that the “typical” sample is properly randomized.

A pre-defined homogenization time will be determined from earth experiments. We suggest a per-cell mixing time of approximately one minute.

Single cell homogenization is preferable, particularly if we find that some samples require re-mixing. Simultaneous mixing of batches of cells will also be a desirable capability.

REAL-SPACE IMAGING

For selected samples (approximately 2 per sample set below) we will attempt to take (at least) a bright-field image shortly after homogenization.

The magnification for the bulk of the measurements would be 60x to 100x (oil objective). We might try to image 10 to 30 planes of these samples below the surface (as many as permitted by scattering of sample).

In later flights (i.e., Ace-2/3) we will use the confocal mode to image as much of the sample as possible in 3D. The confocal will primarily be used for fluorescently labeled particles. This may require more time than bright-field or DIC, but many fewer samples will utilize this capability.

It may be desirable for images taken at 24 hours (in at least a few of the samples) to be transmitted to earth for evaluation.

TYPICAL SEQUENCE OF FLIGHT EVENTS

- **HOMOGENIZATION**
- **PHASE TRANSFORMATIONS (REAL-SPACE IMAGING, Temperature-control)**

SAMPLE SETS

- **Almost all samples will have a corresponding identical system and experiment on earth with which to compare.**
- **In the following we define sample sets, but the <u>exact number and sample definitions may be modified</u> in response to preliminary growth measurements, and in response to work in the scientific community prior to flight.**
- **Ideally, want as many samples as possible!**
- **For Ace-1A, NIPA core-shell particles will not be used. For situations wherein temperature control is available, particles with NIPA will be used.**

SAMPLE SET 1: Cubatic Experiments. PMMA or Polystyrene or Silica particles in water at volume fractions between 0.3 and 0.7. Number of samples in this set would be of order 4 to 6 (for Ace-1A). Fewer samples are needed for Ace-1B, because the NIPA shell permits us to change volume fraction with temperature.

SAMPLE SET 2: 3D Disorder-induced Crystal-to-Glass Transitions. PMMA or Polystyrene or Silica particles in water at volume fractions between 0.4 and 0.7. Number of samples of order 4 to 6 (for Ace-1A). Fewer samples are needed for Ace-1B, because the NIPA shell permits us to change volume fraction with temperature.

SAMPLE SET 3: 3D Jamming, Structural Signatures. PMMA or Polystyrene or Silicaparticles in water at volume fractions between 0.4 and 0.7. Number of samples of order 4 to 6 (for Ace-1A). Fewer samples are needed for Ace-1B, because the NIPA shell permits us to change volume fraction with temperature.

SAMPLE SET 4: OTHER EXPERIMENTS I. PMMA or Polystyrene ellipsoidal particles in water at volume fractions between 0.4 and 0.7. Number of samples of order 4 to 6 (for Ace-1A). Fewer samples are needed for Ace-1B, because the NIPA shell permits us to change volume fraction with temperature.

SAMPLE SET 5: OTHER EXPERIMENTS II. Core-shell NIPA PMMA or Polystyrene particles in oil/water mixtures at volume fractions between 0.2 and 0.7. Surfactants (SDS) are also needed.

Science Requirements

1. SAMPLES, SAMPLE CELLS & MANIPULATION

Particle sizes	400 nm to 3 microns (expected to be viewed or imaged)
Volume fractions	Typically between 0.4 and 0.7 with an accuracy of +/- 2.5%.
Particle densities	Between 1.0 (water) and 2.0 g/cm^3.
Particle refractive indices	In the visible, the index of refraction is between 1.0 (air) and 1.7.
Particle size dispersity	Typically less than 4% (1 SIGMA criterion, meaning if the particle size quoted is "x", the actual size should be in the range "x +/- 2% of x").

Background fluids

Water, PDMS, or an aqueous-based immersion liquid.

Sample homogenization:	Individual cell homogenization should be possible; must not inhibit science work after task is done. (e.g., we must get mixer driver out of the way and park the stir bar.)
1. Magnetic stir bar	1. Care should be taken not to scratch the patterns on one of the cell walls.
2. Temperature	2. When temperature control is available and NIPA-containing particles are used, it is easy to homogenize samples by raising temperature so that colloidal structures melt.

Temperature control 15-35° C ± 0.5° C

- The NIPA-containing particles are sensitive to temperature. This is how we use them to control sample volume fraction. The quoted 15-35 degrees C with 0.5 degrees C stability should be adequate for these studies. An improvement to 0.2 would be better for us, but is not critical. nature of the large particles, small species and background fluids drive the temperature control considerations. Normal pressures and temperatures of the cabin environment should suffice for the samples.
- For the pure solvents the temperature should remain above freezing (>-40° C) and below boiling (<190° C) and such that volume changes do not damage the cells. It would be best and perhaps simplest to require the temperature surrounding the experimental samples be controlled at (25 ± 1)° C.

Tolerance of vibration (g) levels

The surface and the bulk crystals are not expected to survive the g-levels when brought back to earth, but should survive nominal vibrations (10^{-3} g AC or 10^{-6} DC, and 10^{-1} momentary thrust/kicks).

- **For the instrument as a whole, the dc component of gravity is most important for this work. An experiment must be long in duration, but needs no better than 10^{-3} g, averaged over an hour. However, the samples must not be jarred after homogenization and prior to the spectrophotometry. If a crystallized sample is disturbed, its opalescence will disappear. Accelerations greater than 10^{-3} could disrupt the ordered domains. The limit on acceptable average acceleration is given by: $g_{ave} = 10^{-3} * (1/\tau)^{0.5}$, where g_{ave} is the allowable average acceleration, and τ is the time frame of interest, expressed in units of hours. Therefore, over a 1-hour time frame the allowable average acceleration measured at the sample cell is 1 milli-g. Since the vibration environment cannot be controlled, measurement of the vibrational environment during the mission should provide enough information to determine if samples were disturbed during critical periods.**

CELLS

Cell geometry	From 1.0 to 5.6 mm diameter, 0.02 - 0.5 mm thick, ± 10% on dimensions, rectangles easier, but can work with disks.
Number of cells	About 8-10 for space and 100 for ground based studies.

- It is essential that our cell platens can contain enough samples to make the studies proposed here possible. Since the sample volumes required for microscopy are so small, it should be possible to put many sample cells onto a single platen.
- Most of the sample cells could be covered by a single piece of cover slip glass, defining the upper wall of the cells.

EXPERIMENTAL TECHNIQUES/DIAGNOSTICS SPECIFICATIONS

OPTICAL IMAGING (Real space imaging)

White light source	Require for Brightfield epi- and transmission imaging using Kohler illumination.
Excitation for fluorescence	Arc lamp or Laser (532 nm or similar) Used for 3D confocal imaging and also standard fluorescence imaging. Avoid speckle.
Confocal	Desirable for future generation experiments. Primarily to view nearly index matched fluorescent particles. But also can be used in with index contrast (though not as well).

OPTICAL IMAGING (continued)

Depth of imaging in turbid media	Should be able to resolve at depths of about 10-50 microns into the samples for near index-matched particles.
High magnification and resolution	Large particle centroid resolution to 5-20 nm in x, y, and z coordinates. Suggested objectives: 10X (for coarse adjustment it may be desirable), 60X, 100X, and appropriate condensors. Oil immersion objective at 100x.
Field of view	(60-100 microns)^2 up to entire sample cell.
Camera	High-resolution color camera. Digital video recording. Video rates: 30 Hz. Capability for some near real time downlink of video images to for alignment.

On-Board Data Storage Requirements:

- All visual images, and other such data should be stored with a record of the experimental conditions, such as the time the measurement was made, length of measurement, and temperature. It would also be prudent to record information about the settings of the microscope objective and filters, the camera settings, the position of the sample fiducial mark, etc.
- Temperature is to be recorded with each set of data and any changes in temperature during quiescent periods should be recorded whenever the temperature changes by more than 0.1° C.
- Accelerations in excess of 10^{-3} g should be recorded and time-tagged for comparison with data from the experiment.

On-Board Data Storage Requirements:

- Collected data should be time-tagged to MET and GMT with an accuracy of ± 1 minutes.
- Still digital images of samples are desired just before and after homogenization and periodically thereafter.
- Desirable capability is to periodically down-link any of the above data. For example, we can begin analyzing the reflection data or the real-space images. This analysis could in principle give us information relevant to subsequent sample choices, etc.
- Desirable capability for some near real time downlink of video images to allow for alignment. The image quality should have a sufficient resolution with respect to the fiducial in order for us to confirm that the microscope is in focus.

Astronaut Involvement and Experiment Activation

Minimal astronaut involvement is envisioned. This would be required for loading of the sample platens initially, for unloading the samples, and then (optional) in some cases for reloading the samples.

Telepresence

Down-linked color or monochrome CCD images of the samples are desirable just before and after mix/melting. Color or monochrome images are also required at various stages. This will enable the PI to examine state of the sample to assess whether equilibration has occurred.

Post-flight Data Deliverables

1. Copies of all scripts run.
2. All CCD sample images with time-stamps. (In standard (commonly used formats e.g. TIFF, etc.)
3. All particle-tracking / Image-tracking data with time-stamps. (In standard (commonly used formats e.g. TIFF, etc.)
4. Experimental timeline indicating for example, when lenses are optically aligned, etc.
5. History of various settings, such as, illumination source wavelength and power (when used), filter settings for fluorescence cubes (when used), etc.
6. SAM's data (gravitational acceleration monitoring) in a useful format (e.g. - a graphical plot in addition to CDs full of acceleration data would help us in making use of acceleration information).

Significant Success (Criteria)

We have defined a set of operations and samples for these experiments:

* HOMOGENIZATION
* REAL-SPACE IMAGING of Equilibrated Samples
* IN 8 SAMPLE SETS

NOTE: The loss of sample homogenization would be a significant disaster to the mission.

Minimal Success

We have defined a set of operations and samples for these experiments:

* HOMOGENIZATION
* REAL-SPACE IMAGING of Equilibrated Samples
* IN 4 SAMPLE SETS

Advanced Colloids Experiment

LΦCA (Phase 2) Science Concept Review

June 14, 2011